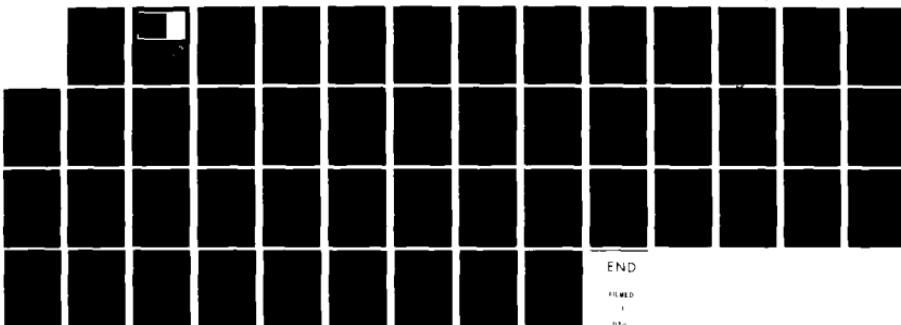
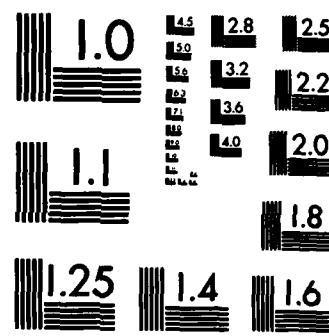


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THE VISCOSITY-CAPILLARITY  
ADMISSIBILITY CRITERION FOR  
SHOCKS AND PHASE TRANSITIONS

R. Hagan and M. Slemrod

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FOR SHOCKS AND PHASE TRANSITIONS

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ABSTRACT

This paper considers admissibility criteria for non-linear conservation laws based on (i) viscosity and (ii) capillarity and viscosity. It is shown by means of specific examples that while (ii) yields results consistent with experiment for materials exhibiting phase transitions, e.g. a van der Waals fluid, (i) does not.

AMS (MOS) Subject Classifications: 80A10, 76T05, 76N99, 35B99, 35M05, 35L65,

35L67

Key Words: phase transitions, van der Waals fluid, admissibility criterion, shocks, traveling waves

Work Unit Number 2 - Physical Mathematics

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## SIGNIFICANCE AND EXPLANATION

In the study of phase transitions in fluids a typical model is provided by the equilibrium configuration of a van der Waals fluid. Such equilibria show a fluid may exist in two phases, liquid and vapor. In this paper we consider criteria which should admit the "physically relevant" liquid-vapor shock wave interfaces. It is shown that a criterion based on both interfacial capillarity and viscosity yields results consistent with experiment for isothermal motions.

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THE VISCOSITY-CAPILLARITY ADMISSIBILITY CRITERION  
FOR SHOCKS AND PHASE TRANSITIONS

R. Hagan\* and M. Slemrod\*

To Jerry Erickson on the occasion of his 60th birthday.

0. Introduction

In a recent paper Serrin [1] reconsidered Korteweg's theory of capillarity [2], [3] and applied it to find conditions for equilibrium of liquid and vapor phases in a van der Waals fluid. In subsequent papers Slemrod [4], [5] extended Serrin's approach and proposed Korteweg's theory as a natural way of choosing physically meaningful solutions for dynamic changes of phase in a van der Waals fluid. In turn James [6] has shown that the Korteweg theory is also a rational way of studying dynamic changes of phase in non-elasticity as well, e.g. in materials exhibiting "martensitic" or "shape memory" phase transitions (see Erickson [7]). In this paper we carry this program one step further: We propose the Korteweg theory to provide the universal admissibility criterion for isothermal motions of compressible thermo-elastic fluids. Indeed it is our belief that the Korteweg theory combined with the introduction of the natural thermal dissipation of heat conduction should provide the universal admissibility criterion for compressible thermo-elastic fluids in general. For the purposes of this paper, however, we restrict ourselves to the isothermal case. We shall show by specific examples when the theory agrees and disagrees with predictions

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based on viscosity alone. Furthermore we will point out the power of the Korteweg theory in choosing admissible singular surfaces for conservation laws which are neither genuinely non-linear nor even hyperbolic, e. g. motion of a van der Waals fluid.

The paper is divided into four sections. The first section derives the balance laws of compressible fluid mechanics in Lagrangian form. The second section discusses admissibility with respect to viscosity alone. The third section considers admissibility with respect to the viscosity-capillarity condition as derived from Korteweg's theory. In particular we show that the usually accepted ideas on admissibility of shocks in ideal gases are consistent with the viscosity-capillarity condition. Finally the fourth section applies the viscosity-capillarity condition the the issue of phase transitions in a van der Waals fluid.

We note that recently Shearer [19] has also made a study of the viscosity and viscosity-capillarity criteria. Basically his work centers on what is here given in Examples 5 and 6 of Section 3. Aside from this overlap our paper is devoted to issues not considered in [19].

## 1. Preliminary discussion of the equations of compressible fluid flow.

We follow the presentation of Courant and Friedrichs [8] of a Lagrangian description based on the law of conservation of mass. The fluid flow is thought of as taking place in a tube of unit cross section along the  $x$ -axis. We attach the value  $X = 0$  to any definite "zero" section moving with the fluid. For any other section we let  $X$  be equal in magnitude to the mass of the fluid in the tube of unit cross sectional area between that section and the zero section. Analytically the quantity  $X$  satisfies the relation

$$X = \int_{X(0,t)}^{X(x,t)} \rho(x,t) dx . \quad (1.1)$$

Here  $\rho(x,t)$  denotes the density of position  $x$  and time  $t$  and  $x = X(x,t)$  denotes the position of the particle so that a mass  $X$  of fluid is enclosed in the tube bounded by  $X(x,t)$  and  $X(0,t)$ . Differentiation of (1.1) implies  $1 = X_x(x,t)\rho(X(x,t),t)$ . Let  $\rho(X(x,t),t) = \tilde{\rho}(x,t)$ ,  $w(X,t) = \tilde{\rho}(x,t)^{-1}$  (the specific volume),  $\dot{x}(x,t) = u(X,t) = X_t(x,t)$  (the velocity).

We denote the stress by  $\tau$ , the specific internal energy by  $\epsilon$ , the specific heat absorption by  $q$ , the heat flux by  $h$ , the specific body force by  $b$ . Then the equations of balance of linear momentum, energy, and mass become

$$\begin{aligned} \ddot{\rho x} &= \tau_x + \rho b , \\ \dot{\rho \epsilon} &= \rho q + \tau \dot{x}_x + h_x , \\ \dot{\rho} + \rho \dot{x}_x &= 0 , \end{aligned}$$

where  $\cdot = \frac{d}{dt}$ . We now apply the chain rule and rewrite this system in the terms of the independent variables  $x, t$  to obtain

$$\begin{aligned} x_{tt} &= \tau_x + b , \\ \epsilon_t &= q + \tau x_{tx} + h_x , \\ (\tilde{\rho} x)_t &= 0 , \end{aligned} \quad (1.2)$$

where we have used the fact that  $\dot{\rho}(x,t) = \tilde{\rho}_t(x,t)$ . The third of these equations is automatically satisfied since  $\tilde{\rho}x_x = 1$ .

The above set of balance laws must be supplemented by constitutive relations. We assume the fluid is compressible, isotropic, and thermo-elastic where the stress, internal energy, and heat flux satisfy

$$\begin{aligned}\tau &= -\pi(w,T), \\ \epsilon &= \hat{\epsilon}(w,T), \\ h &= \hat{h}(w,T), \\ s &= \tilde{s}(w,T), \\ \psi &= \hat{\psi}(w,T),\end{aligned}\tag{1.3}$$

where  $\pi$  (the pressure) and  $\hat{s}$  (the specific entropy) are deriveable from the Helmholtz free energy potential

$$\pi = -\frac{\partial \hat{\psi}}{\partial w}, \quad s = -\frac{\partial \hat{\psi}}{\partial T}.\tag{1.4}$$

We now make the simplifying hypothesis that the fluid is imbedded in a "heat bath" so that the motion is isothermal ( $T = \text{positive constant}$ ) and that there are no body forces. Mathematically this means that  $q$  is assumed to be adjusted so that (1.2a) is always satisfied identically with  $T = \text{constant}$  and  $b \equiv 0$ .

If the motion is isothermal  $\pi(w,T)$  is a function of  $w$  alone and we set  $\pi(w,T) = p(w)$ . Hence (1.2) is equivalent to the first order system

$$\begin{aligned}u_t &= -p(w)_x, \\ w_t &= u_x,\end{aligned}\tag{1.5}$$

where we assume  $p \in C^2(0, \infty)$ . As is easily seen (1.5) is either hyperbolic or elliptic depending on the sign of  $p'(w)$ .

A  $C^1$  curve  $\Gamma : x = \sigma(t)$  across which  $u, w$  experience jumps is called a singular surface or shock wave. If  $\Gamma$  is a singular surface let

$(\sigma(\bar{t}), \bar{t})$  be a fixed point on the graph of  $\Gamma$  and let  $U = \dot{\sigma}(\bar{t})$ . Denote by  $u_+, w_+, u_-, w_-$  the respective limits from the right and the left as  $(x,t) \rightarrow (\sigma(\bar{t}), \bar{t})$  for  $(u,w)$ . If we put  $[u] = u_+ - u_-, [w] = w_+ - w_-, \text{ etc.}$  then we known the Rankine-Hugonot jump conditions must be satisfied across  $\Gamma$ , i.e.

$$\begin{aligned} U[u] - [p] &= 0 \\ U[w] + [u] &= 0 \end{aligned} \quad (1.6)$$

Of course (1.6) implies  $U^2$  satisfies the equation

$$U^2 = - \frac{[p]}{[w]} .$$

2. Admissibility with respect to the viscosity criterion.

Let us imbed the inviscid equations (1.5) in a viscous formulation, i.e. we take

$$\tau = -p(w) + \mu u_x \quad (2.1)$$

where  $\mu > 0$  is the (assumed constant) viscosity.

Now let  $\Gamma : x = \sigma(t)$  be a singular surface for (1.6). We ask the question: Are solutions of (1.5) in the neighborhood of the singular surface  $\Gamma$  limits of solutions (1.2a), (2.1) as  $\mu \rightarrow 0+$ ? While this problem has a long history dating back to Rayleigh [9] it is the more recent discussions of Wendroff [10] and Dafermos [11] we shall follow.

Let  $(\sigma(\bar{t}), \bar{t})$  be a fixed point on the graph of  $\Gamma$  and let  $u_+, w_+, u_-, w_-$ ,  $U$  be as in Section 1. We look for a traveling wave solution of (1.2), (2.1) given by

$$u(x,t) = u(\xi), \quad w(x,t) = w(\xi), \quad \xi = \frac{x-Ut}{\mu} .$$

It follows that  $\hat{u}, \hat{w}$  must satisfy

$$\begin{aligned} -U\hat{u}' &= (-p + \hat{u}')' , \\ -U\hat{w}' &= \hat{u}' , \end{aligned} \quad (2.2)$$

where  $' = \frac{d}{d\xi}$ .

In order for  $\hat{u}, \hat{w}$  to approximate the discontinuous profile of the solution to (1.5) we require

$$(\hat{u}(-\infty), \hat{w}(-\infty), \hat{u}(+\infty), \hat{w}(+\infty)) = (u_-, w_-, u_+, w_+) . \quad (2.3)$$

Definition 2.1. If there exists  $\hat{u}, \hat{w}, c^1$  functions so that (2.2), (2.3) are satisfied for all points  $(\sigma(\bar{t}), \bar{t})$  we say the singular surface satisfies the viscosity admissibility criterion.

Theorem 2.2. The viscosity admissibility criterion is satisfied if and only if

$$-U^2 + \left( \frac{-p(\bar{w}) + p(w_-)}{w-w_-} \right) > 0 \quad (< 0) \quad \text{if } U > 0 (< 0) \quad (2.4)$$

for every value  $\bar{w}$  between  $w_-$  and  $w_+$ .

In other words for  $(w_+ - w_-)U > 0$  ( $(w_+ - w_-)U < 0$ ) the chord which joins  $(w_-, p(w_-))$  to  $(w_+, p(w_+))$  lies above (below) the graph of the function  $p(\bar{w})$  for  $\bar{w}$  between  $w_-$  and  $w_+$ .

Proof. Integrate (2.2) from  $-\infty$  to  $\xi$ . It then easily follows that  $\hat{w}(\xi)$  satisfies the first order equation

$$U^2(\hat{w}(\xi) - w_-) + p(\hat{w}(\xi)) - p(w_-) = -U\hat{w}'(\xi) . \quad (2.5)$$

If  $U \neq 0$  and  $w_- < w_+$  ( $w_- > w_+$ ) then we must have  $w'(\xi) > 0$  ( $w'(\xi) < 0$ ) and hence (2.4) follows.  $\square$

In the exceptional case of a static singular surface where  $U = 0$  we have  $\xi = X/U$  and (2.2) becomes  $p(\hat{w}(\xi))' = 0$ . So if  $\hat{w}$  is a  $C^1$  function satisfying  $\hat{w}(-\infty) = w_-$ ,  $\hat{w}(+\infty) = w_+$  we see  $p(\hat{w}(\xi)) = p(w_-) = p(w_+)$  for all  $-\infty < \xi < \infty$  and hence  $p(\bar{w})$  must equal  $p(w_-) = p(w_+)$  for all  $\bar{w}$  between  $w_-$  and  $w_+$ . So unless  $p$  is identically constant on  $[w_-, w_+]$  a static singular surface is never admissible according to the viscosity criterion.

Example 1. Let  $p(w)$  have the graph shown in Figure 1 where  $p' < 0$ ,  $p'' > 0$  for  $w > w_+$ . In this case the chord connecting  $(w_-, p(w_-))$  to  $(w_+, p(w_+))$  lies above the graph of  $p(w)$  and the singular surface  $\Gamma : X = Ut$  with

$$U = +\sqrt{\frac{-p(w_+) + p(w_-)}{w_+ - w_-}} \quad (2.6)$$

is admissible according to the viscosity criterion.

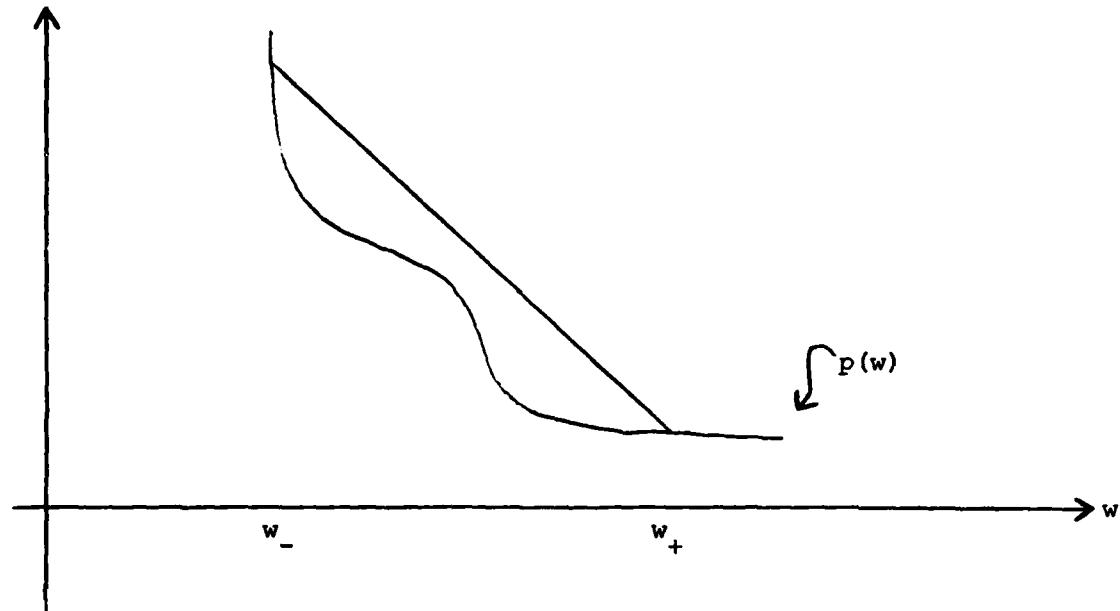


Figure 1

Example 2. Let  $p(w)$  have the graph shown in Figure 2. In Figure 2 the chord joining  $(w_-, p(w_-))$  to  $(w_+, p(w_+))$  again lies above the graph of  $p(w)$  for  $w_- < w < w_+$ , even though the chord is tangent to the graph at  $(w_+, p(w_+))$ . Thus the singular surface  $\Gamma : X = Ut$  with  $U$  given by (2.6) is again admissible according to the viscosity criterion. The purpose of this example is to point out that the viscosity criterion allows for tangency constructions.

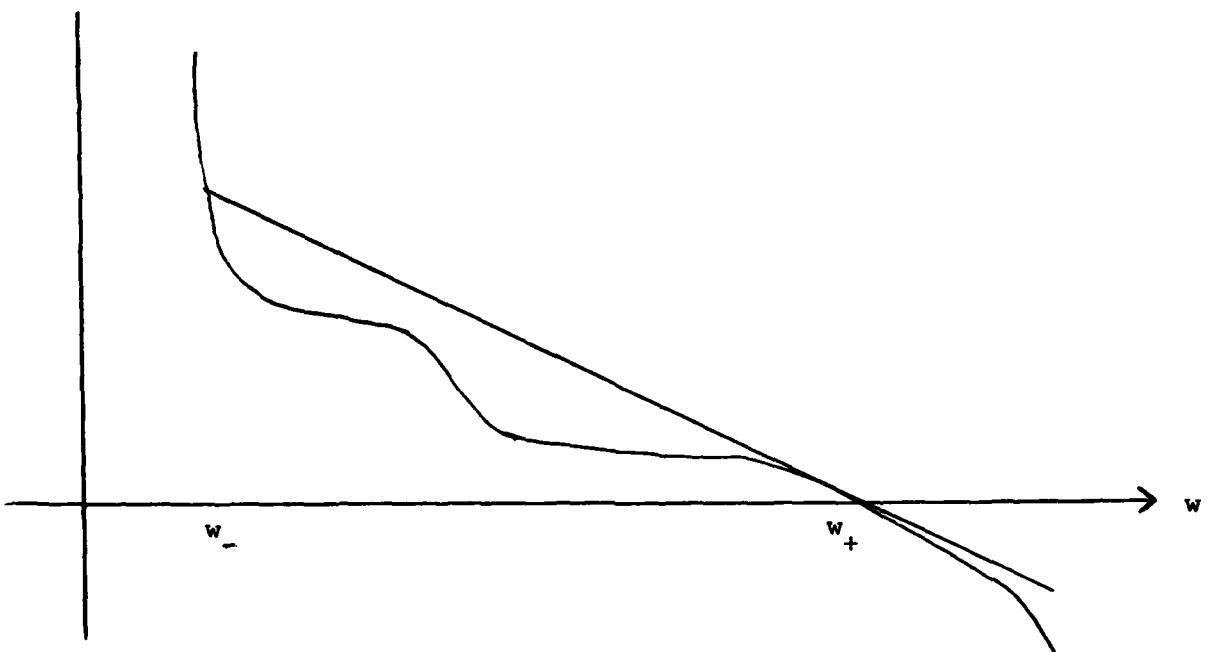


Figure 2

### 3. The viscosity-capillarity criterion

The problem with the viscosity criterion is that it allows only the viscosity as a higher order singular correction in the thermo-elastic fluid's constitutive relation. In line with the generally held belief that consideration of other physically meaningful effects should help pick out the physically relevant solutions. Slemrod [4] suggested a new condition termed the viscosity-capillarity criterion based on Korteweg's theory of capillarity ([2], [3]). In this section we will review the viscosity-capillarity criterion and apply it to some examples.

According to Korteweg's theory the stress  $\tau$  in our one-dimensional, isotropic, isothermal formulation will be given by

$$\tau = p(w) + B(w)w_X^2 - C(w)w_{XX} + \mu(w)u_X . \quad (3.1)$$

For simplicity we shall consider only the constant coefficient case

$$\mu(w) = \mu , \text{ a positive constant,}$$

$$C(w) = \mu^2 A , \text{ A a constant,}$$

$$B(w) = -\mu^2 D , \text{ D a constant.}$$

In this special case (1.2a), (3.1) become

$$u_t = (-p(w) - \mu^2 A w_{XX} + \mu u_X - \mu^2 D w_X^2)_{,X} , \quad (3.2)$$

$$w_t = u_X .$$

Now again let  $\Gamma$  be a singular surface with  $\sigma(t)$ ,  $U$ ,  $w_-$ ,  $w_+$ ,  $u_-$ ,  $u_+$  as given in Section 1. Again we look for traveling wave solutions

$$u(X,t) = \hat{u}(\xi) , w(X,t) = \hat{w}(\xi) , \xi = \frac{X-Ut}{\mu} ,$$

this time for equations (3.2). It then follows that  $\hat{u}$ ,  $\hat{w}$  must satisfy

$$-U\hat{u}' = (-p(\hat{w}) - A\hat{w}'' - D\hat{w}'^2 + \hat{u}')' , \quad (3.3)$$

$$-U\hat{w}' = \hat{u}' .$$

In order that  $\hat{u}, \hat{w}$  will approximate the discontinuous profile we require again that

$$(\hat{u}(-\infty), \hat{w}(-\infty), \hat{u}(+\infty), \hat{w}(+\infty)) = (u_-, w_-, u_+, w_+) . \quad (3.4)$$

These considerations motivate the following definition, where from now on we drop the  $\hat{\cdot}$  superscript.

Definition 3.1. If there exist  $u \in C^2, w \in C^3$  satisfying (3.3), (3.4) for all points  $(\sigma(\bar{t}), \bar{t})$  we will say the singular surface  $\Gamma$  satisfies the viscosity-capillarity admissibility criterion (A,D).

Since the criterion may possibly be satisfied for one (A,D) pair and not another the dependence of the criterion on A and D has been explicitly noted in the above definition.

Lemma 3.2. The viscosity-capillarity criterion (A,D) is satisfied if and only if there exists  $w(\xi) \in C^3$  a solution of the second order equation

$$Aw'' + Uw' + Dw'^2 + f(w, U) = 0 , \quad (3.5)$$

$$w(-\infty) = w_-, w(+\infty) = w_+ , \quad (3.6)$$

where

$$f(\zeta, U) \doteq U^2(\zeta - w_-) + p(\zeta) - p(w_-) . \quad (3.7)$$

Proof. Integrate (3.3) from  $-\infty$  to  $\xi$ . □

Theorem 3.3. Assume (3.5) possesses precisely two equilibrium point  $w = w_-$ ,  $w' = 0$  and  $w = w_+$ ,  $w' = 0$  with  $w_- < w_+$ ,  $p'(w_-) < 0$ ,  $p'(w_+) < 0$ . Then there is a solution  $w(\xi)$  of (3.5) connecting these equilibrium points if the following holds:

(i)  $A > 0$ ,  $U > 0$  and

$$(a) (-p'(w_+))^{\frac{1}{2}} < U < (-p'(w_-))^{\frac{1}{2}} ,$$

(b) the chord connecting  $(w_-, p(w_-))$  and  $(w_+, p(w_+))$  lies above the graph of  $p(w)$  for  $w_- < w < w_+$ ,

(c) for some  $\ell > w_+$ ,  $\int_{\ell}^{w_-} \exp(\frac{2D}{A} \zeta) f(\zeta, U) d\zeta = 0$  ;

(ii)  $A > 0, U < 0$  and

(a)  $-(-p'(w_+))^{1/2} < U < -(-p'(w_-))^{1/2}$ ,

(b) the chord connecting  $(w_-, p(w_-))$  to  $(w_+, p(w_+))$  lies below the graph of  $p(w)$  for  $w_- < w < w_+$ ,

(c) for some  $\ell < w_-$ ,  $\int_{\ell}^{w_-} \exp(\frac{2D}{A} \zeta) f(\zeta, U) d\zeta = 0$  ;

(iii)  $A < 0, U < 0$  and

(a)  $(-p'(w_+))^{1/2} < -U < (-p'(w_-))^{1/2}$ ,

and i-b, ii-c hold;

(iv)  $A < 0, U > 0$  and

(a)  $-(-p'(w_+))^{1/2} < -U < -(-p'(w_-))^{1/2}$ ,

and ii-b, i-c hold.

Proof. Rewrite (3.5) in first order form

$$\begin{aligned} w' &= v, \\ Av' &= -f(w, U) - Uv - Dv^2, \end{aligned} \tag{3.8}$$

and set

$$H(w, v) = \exp(\frac{2D}{A} w)v^2 + G(w, U), \text{ where}$$

$$G(w, U) = \frac{2}{A} \int_{w_+}^w \exp(\frac{2D}{A} \zeta) f(\zeta, U) d\zeta.$$

Let  $\Omega = \{(w, v); w_- < w < \ell, H(w, v) < H(w_-, 0)\}$

$$= \{(w, v); w_- < w < \ell, \exp(\frac{2D}{A} w)v^2 < \frac{2}{A} \int_{w_-}^w \exp(\frac{2D}{A} \zeta) f(\zeta, U) d\zeta\}$$

where  $\ell$  is now assumed to be the smallest such  $\ell$  so that i-c holds. From i-b and i-c we see  $\Omega$  is a simply connected bounded open set in  $\mathbb{R}^2$  containing  $(w_+, 0)$ . Furthermore

$$\frac{dH}{d\zeta} = -\frac{2}{A} U \exp(\frac{2D}{A} w)v^2 < -\text{const. } v^2 \text{ for const. } > 0$$

where  $(w, v) \in \bar{\Omega}$ . Thus any orbit which enters  $\Omega$  remains in  $\Omega$ . Also i-a

shows  $(w_-, 0)$  is a saddle and an elementary analysis of this saddle shows that it possesses an unstable manifold which enters  $\Omega$ . By LaSalle's invariance principle ([12], p. 316) an orbit entering  $\Omega$  on this manifold must approach an equilibrium point since  $H$  is a Liapunov function on  $\Omega$ . Such an orbit cannot approach  $(w_-, 0)$  since  $\frac{dH}{d\zeta} < 0$  in  $\Omega$  and  $H(w, v) < H(w_-, 0)$  for  $(w, v)$  in  $\Omega$ , hence it approaches  $(w_+, 0)$ .

(ii) The proof here is analogous to (i) with

$$G(w, U) = \frac{2}{A} \int_{w_-}^w \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, U) d\zeta .$$

The saddle now is at  $(w_-, 0)$  and  $\Omega = \{(w, v); l < w < w_+, H(w, v) < H(w_+, 0)\}$  where  $l$  is assumed to be the largest such  $l$  so that ii-c holds.

(iii) The proof is analogous to (i) with  $G$  and  $\Omega$  as given in (ii).

(iv) Again the proof is analogous to (i) with  $G$  and  $\Omega$  as given in (i).

Corollary 3.4. (i) The conclusion of Theorem 3.3(i) holds if i-c is replaced by (i-c'):  $p'' > 0$  for  $w > w_+$ .

(ii) The conclusion of Theorem 3.3(ii) holds if ii-c is replaced by (ii-c'):  $p'' < 0$  for  $w < w_-$ .

Proof. (i) We note (i-c') implies  $p'(w) - p'(w_+) > 0$  for  $w > w_+$  and hence by i-a  $p'(w) + U^2 > \epsilon$  for some  $\epsilon > 0$ . Thus  $p(w) - p(w_+) + U^2(w-w_+) > \epsilon(w-w_+)$  for  $w > w_+$  and  $\int_{w_-}^{w_+} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, U) d\zeta + \infty$  as  $w \rightarrow +\infty$ . Hence there is an  $l$  so that

$$\int_l^{w_+} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, U) d\zeta = 0, l > w_+ .$$

(ii) The proof is similar to (i). □

Corollary 3.5. If  $p' < 0$ ,  $A > 0$  and i-a holds then the conclusion of Theorem 3.3(i) holds.

Proof. Apply Corollary 3.4. □

Corollary 3.6. If  $p' < 0$ ,  $p'' > 0$ ,  $A < 0$  and  $\lim_{w \rightarrow 0^+} \int_w^{w_-} p(\zeta) d\zeta = +\infty$  then the conclusion of Theorem 3.3(iii) holds.

Proof. Here i-b, i-d are automatically satisfied and the rest is an obvious application of Theorem 3.3(iii). □

Example 3. Consider an ideal gas with constitutive relation  $\pi(w, T) = RTw^{-1}$  where  $R$  is a positive constant. As the chord joining  $(w_-, p(w_-))$  to  $(w_+, p(w_+))$  lies above the graph of  $p(w)$  between  $w_-$  and  $w_+$ , the singular surface  $\Gamma : X = Ut$  with  $U$  given by (2.6) is admissible according to the viscosity condition. Corollary 3.5 shows  $\Gamma$  is also admissible according to the viscosity-capillarity condition (A,D) for  $A > 0$ . On the other hand Corollary 3.6 shows that  $\Gamma : X = Ut$  with

$$U = \sqrt{\frac{-p(w_+) + p(w_-)}{w_+ - w_-}}$$

is admissible according to the viscosity-capillarity condition (A,D) if  $A < 0$ . Thus  $A < 0$  admits rarefaction shocks in an ideal gas. For this reason we view  $A > 0$  as the only physically reasonable choice.

Example 4. Let  $p(w)$  be as in Figure 1. In Example 1 we saw  $\Gamma : X = Ut$  was admissible according to the viscosity criterion where  $U$  is given by (2.7). Now we see by Corollary 3.4(i) that this same  $\Gamma$  is also admissible according to the viscosity-capillarity criterion (A,D),  $A > 0$ .

Example 5. Assume  $p(w)$  has the graph as shown in Figure 2. In this case if  $D = 0$  the potential  $G(w) = \int_{w_+}^w f(\zeta, U) d\zeta$  has the graph shown in Figure 3.

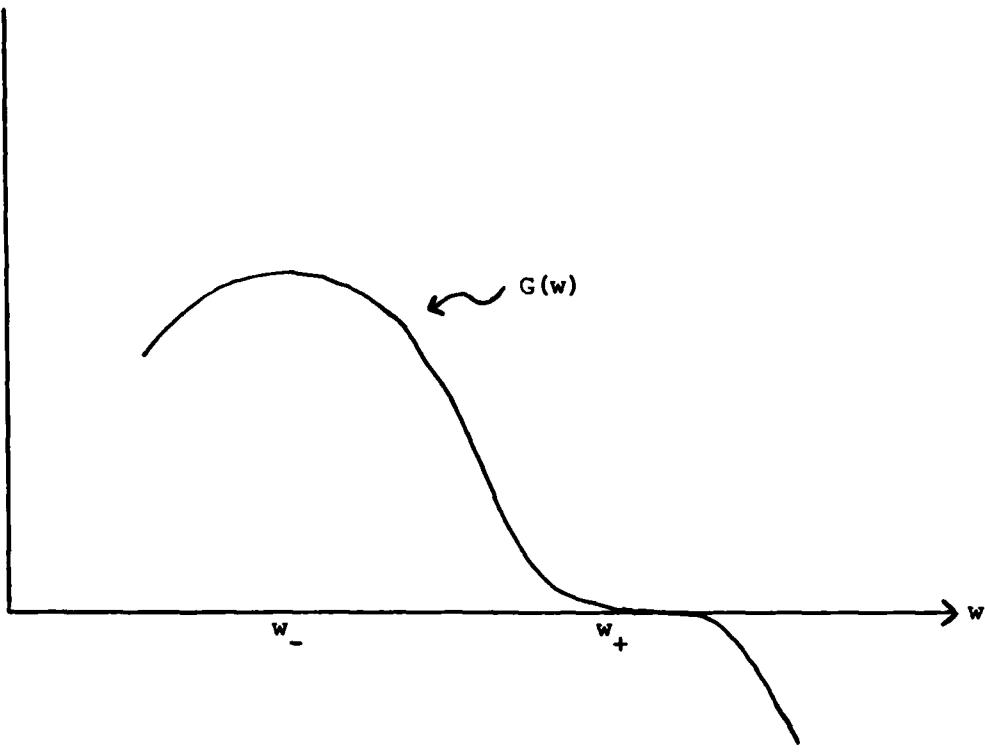


Figure 3

We note the point  $(w_+, G(w_+))$  is a point of inflection. Typical phase flows exiting from  $w = w_-, v = 0$  will generally be unbounded and only in exceptional circumstances will we have  $w(+\infty) = w_+$ . Of course (3.5), (3.6) has the rather simple mechanical analogue. Namely one visualizes a bead rolling down the hill given by the graph of  $G(w)$ . Admissibility according to the viscosity-capillarity criterion ( $A > 0, D = 0$ ) would require the damping force of rolling motion given by  $Uw'$  sufficient to bring the bead to rest at the inflection point  $(w_+, G(w_+))$  - a highly unlikely circumstance. Hence except for this exceptional case the singular surface  $\Gamma : X = Ut$  where  $U$  is given by (2.6) will be admissible according to the viscosity criterion and inadmissible according to the viscosity-capillarity criterion ( $A > 0, D = 0$ ).

Example 6. Let  $p(w)$  be as shown in Figure 5.

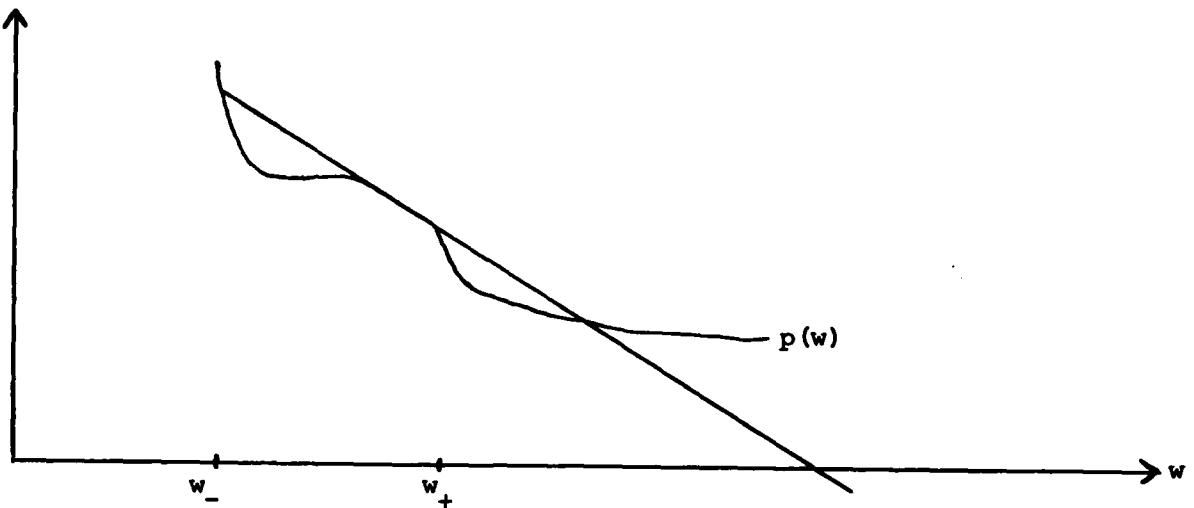


Figure 4

In Figure 4 the chord joining  $(w_-, p(w_-))$  to  $(w_+, p(w_+))$  again lies above the graph of  $p(w)$  for  $w_- < w < w_+$ , even though the chord is tangent to the graph at  $(w_+, p(w_+))$ . So the singular surface  $\Gamma : X = Ut$  with  $U$  given by (2.7) is admissible according to the viscosity criterion. However if we plot the potential  $G(w) = \int_{w_+}^w f(\zeta, U) d\zeta$  we find  $G(w)$  has the graph shown in Figure 5.

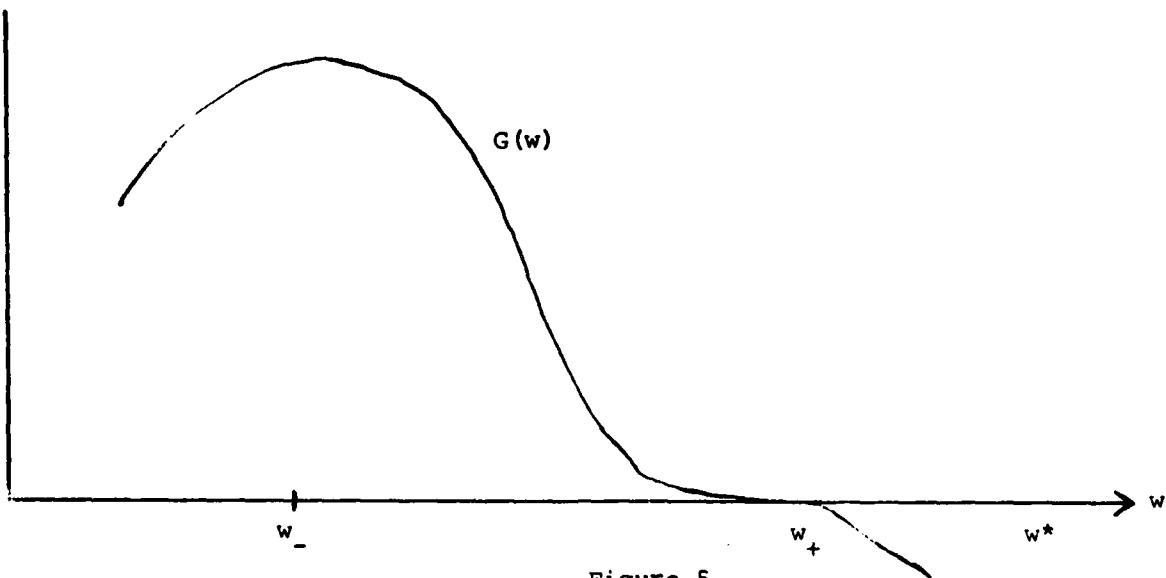


Figure 5

Here again as in Example 4  $(w_+, G(w_+))$  is an inflection point. Now however instead of the typical flows of (3.5) exiting  $w = w_-, w' = 0$  being unbounded these flows will either be unbounded or approach the equilibrium point  $w = w^*, w' = 0$ , modulo the exceptional case that the  $f(w)$  approaches  $w = w^*, w' = 0$ . So again the singular surface  $\Gamma : X = Ut$  with  $U$  given by (2.6) is admissible according to the viscosity criterion and inadmissible (modulo an exceptional case) according to the viscosity capillarity condition  $(A > 0, D = 0)$ .

#### 4. Dynamics of phase transitions in a van der Waals fluid.

In this section we examine the admissibility of singular surfaces for isothermal motions of a van der Waals fluid. In a van der Waals fluid the constitutive relation for the pressure is given by

$$H(w,T) = \frac{RT}{w-b} - \frac{a}{w^2}, \quad 0 < b < w < \infty$$

where  $a, b, R$  are positive constants (see for example [13], [14], [15]).

Again we set  $p(w) = H(w,T)$  for isothermal motions,  $T = \text{positive constant}$ .

For  $T$  sufficiently small  $p(w)$  has a graph as shown in Figure 6.

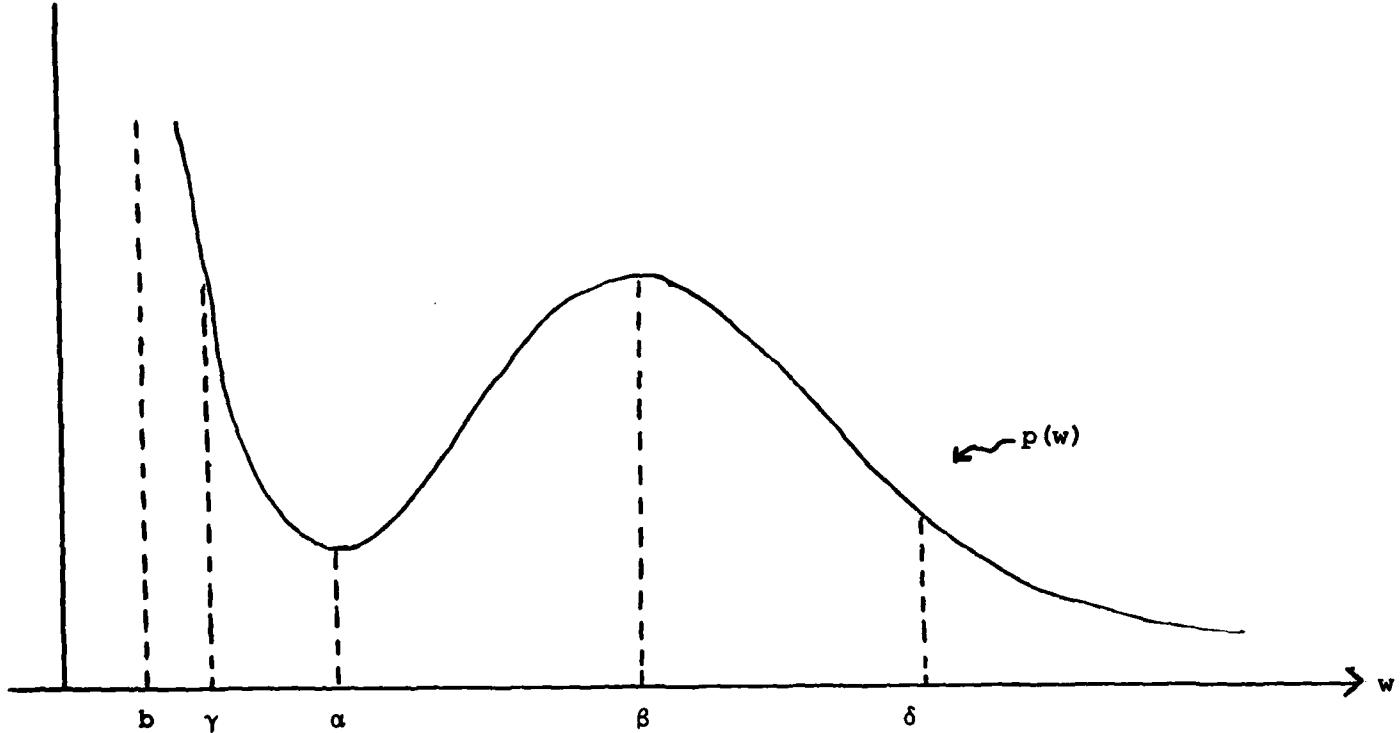


Figure 6

Actually in what follows we shall not require anything so specific as the van der Waals equation of state. Instead we assume  $p(w)$  satisfies the following hypotheses:

(H1)  $p'(w) < 0$  for  $w \in (b, \alpha) \cup (\beta, \infty)$ ,  $b > 0$ ,

(H2)  $p'(\alpha) = p'(\beta) = 0$ ,

(H3)  $p'(w) > 0$  for  $w \in (\alpha, \beta)$  where  $b < \alpha < \beta < \infty$ ,

(H4)  $p(w) > 0$  for  $w \in (b, \infty)$ ,

(H5)  $p \in C^2(b, \infty)$ ,

(H6)  $p(w) < p(\alpha)$  as  $w \rightarrow \infty$ ,

(H7)  $p(w)$  has one inflection point in  $(\beta, \infty)$ ,

(H8)  $p(\gamma) = p(\beta)$ ,  $p(\delta) = p(\alpha)$ ,  $b < \gamma < \alpha$ ,  $\beta < \delta < \infty$ .

The domains  $(b, \alpha)$  and  $(\beta, \infty)$  will be called the  $\alpha$  (liquid) phase and  $\beta$  (vapor) phase respectively.

We shall now consider the admissibility of several singular surfaces separating liquid and vapor phases of a van der Waals fluid.

Example 7. When  $w_{1-}$  and  $w_{1+}$  are as shown in Figure 7 the chord connecting  $(w_{1-}, p(w_{1-}))$  and  $(w_{1+}, p(w_{1+}))$  lies above the graph of  $p(w)$  between  $w_{1-}$  and  $w_{1+}$  as so  $\Gamma : x = U_1 t$  with

$$U_1 = + \sqrt{\frac{-p(w_{1+}) + p(w_{1-})}{w_{1+} - w_{1-}}}$$

is admissible according to the viscosity criterion. Theorem 3.3(i) shows  $\Gamma$  is also admissible according to the viscosity-capillarity condition (A,D),  $A > 0$ .

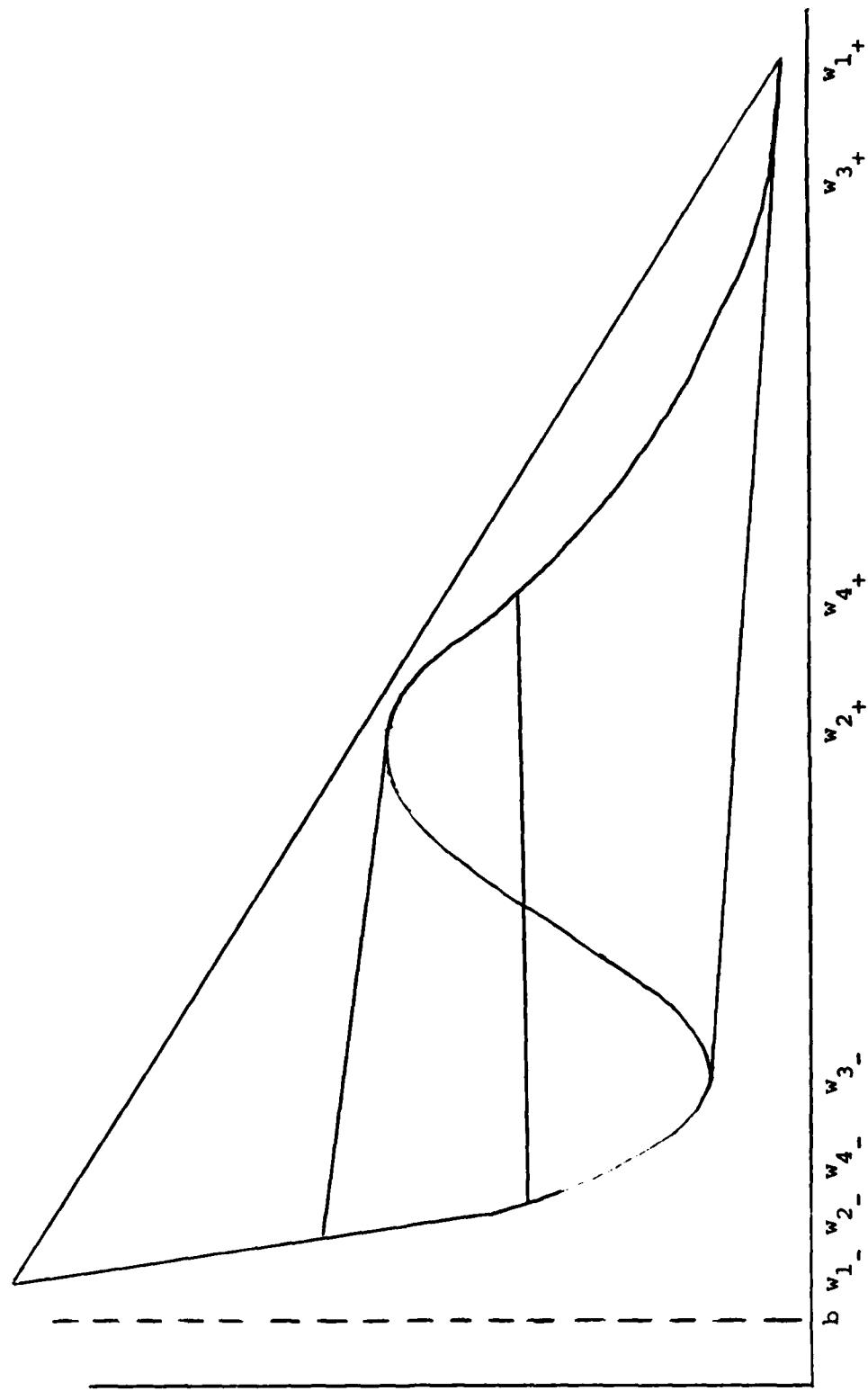


Figure 7

Example 8. When  $w_{2_+}$  and  $w_{2_-}$  are shown in Figure 7 the same chord-graph argument as in Example 7 shows  $\Gamma : x = U_2 t$  with

$$U_2 = + \sqrt{\frac{-p(w_{2_+}) + p(w_{2_-})}{w_{2_+} - w_{2_-}}}$$

is admissible according to the viscosity criterion. However an argument analogous the one of Example 6 shows that (modulo an exceptional circumstance)  $\Gamma$  will not be admissible according to the viscosity-capillarity condition  $(A,D)$ ,  $A > 0$ ,  $D = 0$ . We expect that admissibility according to the viscosity-capillarity criterion will not be aided if  $D \neq 0$ .

Example 9. For  $w_{3_+}$  and  $w_{3_-}$  shown in Figure 7 the remarks made in Example 8 again apply. So  $\Gamma : x = U_3 t$  with

$$U_3 = - \sqrt{\frac{-p(w_{3_+}) + p(w_{3_-})}{w_{3_+} - w_{3_-}}}$$

is admissible according to the viscosity criterion but not generally admissible according to the viscosity-capillarity condition  $(A,D)$ ,  $A > 0$ .

Example 10. For  $w_{4_+}$  and  $w_{4_-}$  shown in Figure 7 the singular surface is  $\Gamma : x = 0$  with  $U_4 = 0$  since  $p(w_{4_-}) = p(w_{4_+})$ . By the remark in Section 2  $\Gamma$  cannot be admissible according to the viscosity criterion. On the other hand an elementary quadrature solution of (3.5), (3.6) shows that if  $w_{4_-}$  and  $w_{4_+}$  satisfy

$$\int_{w_{4_-}}^{w_{4_+}} \exp\left(+\frac{2D}{A}\zeta\right)(p(\zeta) - p(w_{4_-}))d\zeta = 0$$

then  $\Gamma$  is admissible according to the viscosity-capillarity condition (A,D). Of course if  $D = 0$  the above relation reduces to the well known Maxwell equal area rule [1], [13], [14]. If  $D \neq 0$  the relation falls within the new class of "rules" proposed by Serrin [1].

We note that for non-zero  $U$  when the chord connecting  $(w_-, p(w_-))$  and  $(w_+, p(w_+))$  cuts the graph of  $p(w)$  at intermediate value of  $w$ , Theorem 2.2 precludes any such construction being admissible according to the viscosity criterion. Such a construction may however be admissible according to the viscosity-capillarity condition (A,D). We now examine this situation in detail.

Example 11. Let  $w_-$  be given  $(b, \alpha)$  and  $w_+(U)$  be a solution in  $(\beta, \infty)$  of the Rankine-Hugoniot relation with  $U > 0$ , i.e.  $w_+(U)$  satisfies

$$U = + \sqrt{\frac{-p(w_+(U)) + p(w_-)}{w_+(U) - w_-}} .$$

The line  $\Gamma : X = Ut$  defines a singular surface. We consider the admissibility of  $\Gamma$  according to the viscosity-capillarity condition (A,D) when  $f(\zeta, U) = p(\zeta) - p(w_-) + U^2(\zeta - w_-)$  possesses four zeroes, namely  $w_-$ ,  $w_+(U)$  of course, plus two additional zeroes  $\overset{\circ}{w}(U)$ ,  $w^*(U)$  where  $\alpha < \overset{\circ}{w}(U) < \beta < w^*(U) < w_+(U)$ . Thus  $w^*(U)$  is the smallest solution of  $f(\zeta, U) = 0$  in  $(\beta, \infty)$  and  $w_+(U)$  is the solution of  $f(\zeta, U) = 0$  in  $(\beta, \infty)$  which satisfies  $p'(\zeta) + U^2 > 0$ . We also assume  $U^2 < -p'(w_-)$  (see Figure 8).

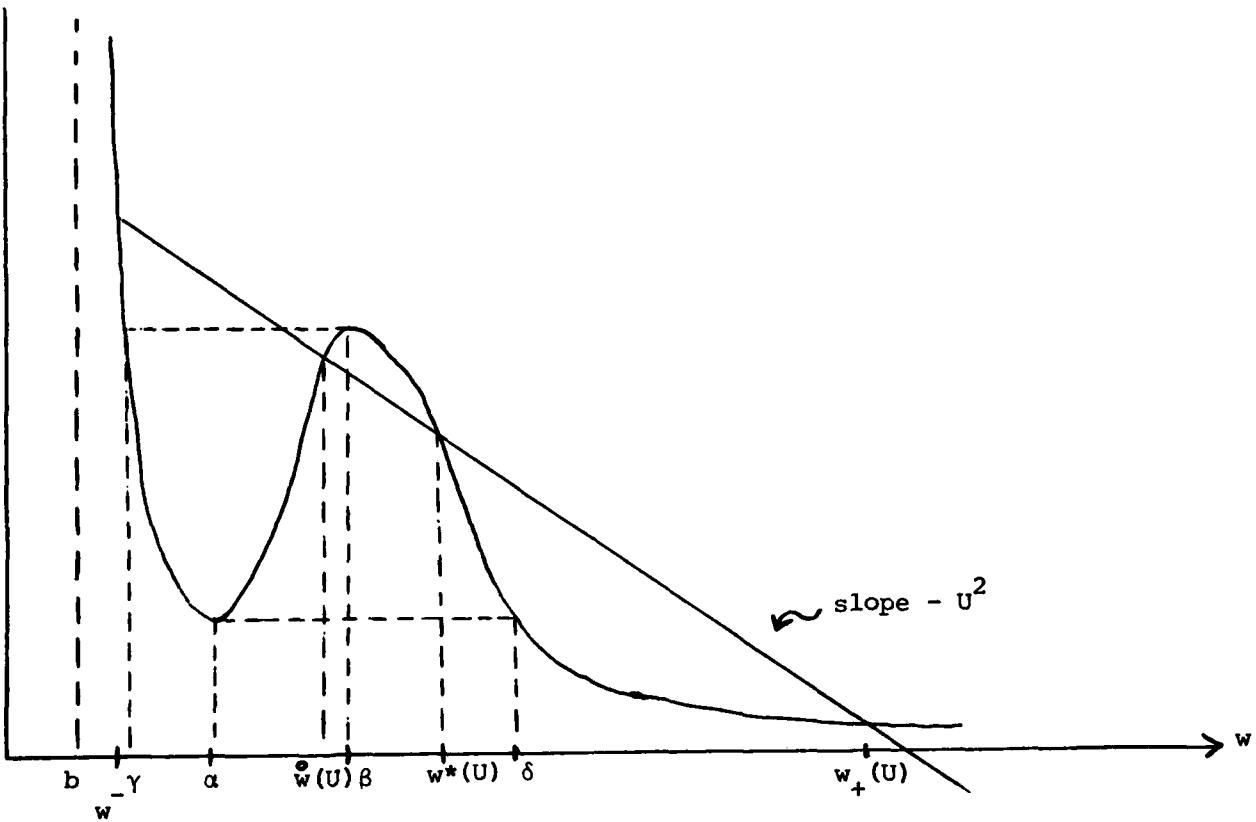


Figure 8

Again the admissibility of  $\Gamma$  according to the viscosity-capillarity criterion (A,D) is equivalent to the existence of a solution of (3.5), (3.6) or equivalently (3.8) with boundary conditions  $(w(+\infty), v(+\infty)) = (w_+(U), 0)$ ,  $(w(-\infty), v(-\infty)) = (w_-, 0)$ . We now state our main theorem.

Theorem 4.1. (i) Let  $A > \frac{1}{8}$ . Then there exists  $\bar{U} > 0$  so that the singular surface  $\Gamma : x = \bar{U}t$  for the solution

$$\begin{cases} w = w_- & w = w^*(\bar{U}) \\ u = u_- & u = u_- - \bar{U}(w^*(\bar{U}) - w_-) \end{cases} \quad x < \bar{U}t, \quad x > \bar{U}t \quad (4.1)$$

of (1.5) is admissible according to the viscosity-capillarity condition (A,D)

if either

$$(I) \quad a > w_- > \gamma \quad \text{and} \quad \int_{w_-}^{w^*(0)} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, 0) d\zeta < 0$$

or

$$(I') \quad b < w_- < \gamma ,$$

and

(II) there exists  $U_M > 0$  so that

$$\int_{w_-}^{w^*(U_M)} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, U_M) d\zeta = 0 .$$

(ii) Let  $A > \frac{1}{8}$ . Assume (I) or (I') and (II) of (i) above hold. Then for all  $U$ ,  $0 < U < \bar{U}$ , the singular surface  $\Gamma : X = Ut$  for the solution

$$\begin{cases} w = w_- & w = w_+(U) \\ u = u_- & u = u_- - U(w_+(U) - w_-) \end{cases} \quad \begin{matrix} x < Ut \\ x > Ut \end{matrix} \quad (4.2)$$

of (1.5) is admissible according to viscosity-capillarity criterion (A,D),  $\bar{U}$  is as given in (i).

The theorem will be proven via a sequence of lemmas.

Lemma 4.2. Let  $U > 0$ ,  $A > 0$ . Then the equilibrium point  $(w_-, 0)$  of (3.8) is a saddle. Furthermore  $\gamma_U^+(w_-, 0)$ , the orbit exiting from the saddle in the  $v > 0$  half plane, either approaches an equilibrium point or crosses the  $w_-$  axis for increasing  $\xi$ .

Proof. Set  $n(w, U) = w'(ξ)$ . From (3.5) we find  $n$  satisfies

$$A n \frac{dn}{dw} + Un + Dn^2 + p(w) - p(w_-) + U^2(w - w_-) = 0 , \quad (4.3)$$

$$n(w_-, 0) = 0 , \quad (4.4)$$

and hence

$$\begin{aligned} n(w, U) &= -\frac{2}{A} U \int_{w_-}^w \exp\left(\frac{2D}{A} (\zeta-w)\right) n(\zeta, U) d\zeta \\ &\quad - \frac{2}{A} \int_{w_-}^w \exp\left(\frac{2D}{A} (\zeta-w)\right) f(\zeta, U) d\zeta . \end{aligned} \quad (4.5)$$

From (H1) - (H6) we know

$$\begin{aligned} f(\zeta, U) &> 0 \text{ on } (b, w_-) \cup (\bar{w}(U), w^*(U)) \cup (w_+(U), \infty) , \\ &< 0 \text{ on } (w_-, \bar{w}(U)) \cup (w^*(U), w_+(U)) . \end{aligned}$$

If the solution exiting from the saddle doesn't cross the  $w$  axis or approach an equilibrium point it must tend to  $+\infty$  as  $\xi \rightarrow +\infty$ . But for such a solution we know from (4.5) that

$$n^2(w, U) < -\frac{2}{A} \int_{w_-}^w \exp\left(\frac{2D}{A} (\zeta-w)\right) f(\zeta, U) d\zeta .$$

So by L'Hôpital's rule  $\lim_{w \rightarrow +\infty} n^2(w, U) < -\frac{2}{A} \lim_{w \rightarrow +\infty} f(w, U) = -\infty$ . Hence  $w$  cannot approach  $+\infty$  and the lemma is proven.

□

Definition 4.3. If  $\gamma_U^+(w_-, 0)$  intersects the  $w$ -axis define  $\tilde{w}(U)$  to be that value of  $w$  so that  $(\tilde{w}(U), 0) \in \gamma_U^+(w_-, 0)$  and  $\tilde{w}(U)$  is the first point of crossing the  $w$ -axis of  $\gamma_U^+(w_-, 0)$ . If  $\gamma_U^+(w_-, 0)$  doesn't intersect the  $w$  axis define  $(\tilde{w}(U), 0)$  to be the equilibrium point approached by  $\gamma_U^+(w_-, 0)$  as  $\xi \rightarrow +\infty$ .

Lemma 4.4. Let  $n(w, U)$  be the solution of (4.3), (4.4). Then for  $A > \frac{1}{8}$ ,  $0 < U_1 < U_2$ , we have  $n(w, U_1) > n(w, U_2)$  on  $(w_-, \tilde{w}(U_2))$ . Furthermore we have  $\tilde{w}(U_2) < \tilde{w}(U_1)$ .

Proof. A direct calculation from (4.3), (4.4) shows

$$\frac{\partial}{\partial U} \frac{\partial}{\partial w} n(w_-, U) = -\frac{1}{2A} + \frac{(1-4A)U}{A(U^2 - 4A(p'(w_-) + U^2))^{1/2}} .$$

Since  $p'(w_-) + U^2 < 0$  we see

$$\frac{\partial}{\partial U} \frac{\partial}{\partial w} \eta(w_-, U) < \frac{1}{2A} - 4 \quad \text{if } 1-4A > 0$$

$$< -\frac{1}{2A} \quad \text{if } 1-4A < 0 .$$

$$\text{Hence } \frac{\partial}{\partial U} \frac{\partial}{\partial w} \eta(w_-, U) < 0 \quad \text{if } A > \frac{1}{8}.$$

Now suppose  $\eta(w, U_1) - \eta(w, U_2)$  has a zero on  $(w_-, \tilde{w}(U_1)) \cap (w_-, \tilde{w}(U_2))$ .

Let  $v$  be the smallest such zero. Then from (4.3) we have

$$A \eta(v, U_1) [\frac{d\eta}{dw}(v, U_1) - \frac{d\eta}{dw}(v, U_2)] = \eta(v, U_1)(U_2 - U_1) + (v - w_-)(U_2^2 - U_1^2) .$$

Since  $U_2 > U_1 > 0$ ,  $v > w_-$ , and  $\eta(v, U_1) > 0$ , we have

$$A \eta(v, U_1) [\frac{d\eta}{dw}(v, U_1) - \frac{d\eta}{dw}(v, U_2)] > 0. \quad \text{Hence } \frac{d\eta}{dw}(v, U_1) > \frac{d\eta}{dw}(v, U_2) \quad \text{which}$$

contradicts the assumption that  $v$  is the smallest zero of

$\eta(w, U_1) - \eta(w, U_2)$ . Thus  $\eta(w, U_1) > \eta(w, U_2)$  on  $(w_-, \tilde{w}(U_1)) \cap (w_-, \tilde{w}(U_2))$  and hence  $\tilde{w}(U_2) < \tilde{w}(U_1)$ .

Definition 4.5. For the first order system (3.8) set

$$G(w, U) = \frac{2}{A} \int_{w_+(U)}^w \exp(\frac{2D}{A} \zeta) f(\zeta, U) d\zeta ,$$

$$H(w, v) = \exp(\frac{2D}{A} w)v^2 + G(w, U), \quad \text{and}$$

$$\Omega_U = \{(w, v); w^*(U) < w, H(w, v) < H(w^*(U), 0)\} .$$

Lemma 4.6.  $\Omega_U$  is a simply connected bounded open set. Furthermore if

$A > 0$ ,  $U > 0$ ,  $w^*(U) < w_+(U)$  any orbit of (3.8) entering  $\Omega_U$  has  $(w_+(U), 0)$  for an  $\omega$ -limit set.

Proof. From (H3), (H4), and (H7) we see there is a unique  $\ell > w^*(U)$  so that  $\int_{w^*(U)}^{\ell} \exp(\frac{2D}{A} \zeta) f(\zeta, U) d\zeta = 0$ . Hence  $\Omega_U$  is simply connected bounded and open. Also since  $\frac{dH}{d\zeta} = -\frac{2v^2}{A} U \exp(\frac{2D}{A} w)$  we see  $\frac{dH}{d\zeta} < -\text{const. } v^2$  for  $\text{const.} > 0$  inside  $\Omega_U$ .

Because any orbit entering  $\Omega_U$  remains in  $\Omega_U$  LaSalle's invariance principle [12] asserts that orbit approaches the only equilibrium point in  $\Omega_U$ , namely  $(w_+(U), 0)$ .

□

Lemma 4.7. Let  $A > 0$ ,  $U > 0$ ,  $w^*(U) < w_+(U)$ . Then the solution of (3.8) exiting from the saddle  $(w^*(U), 0)$  in the  $v > 0$  half plane enters  $\Omega_U$  and has  $(w_+(U), 0)$  for an  $w$ -limit set.

Proof. Linearize about  $(w^*(U), 0)$  and use Lemma 4.6. □

Lemma 4.8. For  $0 < U_1 < U_2$  we have  $\Omega_{U_2} \subset \Omega_{U_1}$ .

Proof. Note  $\Omega_{U_1} = \{(w, v); w^*(U_1) < w, v^2 < -\frac{2}{A} \int_{w^*(U_1)}^w \exp(\frac{2D}{A}\zeta) f(\zeta, U_1) d\zeta\}$ ,

$$\Omega_{U_2} = \{(w, v); w^*(U_2) < w, v^2 < -\frac{2}{A} \int_{w^*(U_2)}^w \exp(\frac{2D}{A}\zeta) f(\zeta, U_2) d\zeta\}.$$

Now for  $0 < U_1 < U_2$ ,  $w^*(U_1) < w^*(U_2)$  and  $f(\zeta, U) = p(\zeta) - p(w_-) + U^2(\zeta - w_-)$  so  $f(\zeta, U_2) > f(\zeta, U_1)$ . Therefore if  $(w, v) \in \Omega_{U_2}$  we have  $w^*(U_1) < w^*(U_2) < w$  and

$$\begin{aligned} v^2 &< -\frac{2}{A} \int_{w^*(U_2)}^w \exp(\frac{2D}{A}\zeta) f(\zeta, U_2) d\zeta < -\frac{2}{A} \int_{w^*(U_2)}^w \exp(\frac{2D}{A}\zeta) f(\zeta, U_1) d\zeta \\ &< -\frac{2}{A} \int_{w^*(U_1)}^w \exp(\frac{2D}{A}\zeta) f(\zeta, U_1) d\zeta. \end{aligned}$$

Hence  $(w, v) \in \Omega_{U_1}$ . □

Lemma 4.9. Assume there exists  $\bar{U} > 0$  so that there is a solution of (3.8) connecting the saddle  $(w_-, 0)$  with the saddle  $(w^*(\bar{U}), 0)$  in the  $v > 0$  half plane,  $w^*(\bar{U}) < w_+(\bar{U})$ . Then there exists  $\epsilon > 0$  so that if  $-\epsilon < U - \bar{U} < 0$ ,  $\gamma_U^+(w_-, 0)$  has  $(w_+(U), 0)$  for its  $w$ -limit set.

Proof. For the orbit  $\gamma_U^+(w^*(\bar{U}), 0)$  exiting from the saddle  $(w^*(\bar{U}), 0)$  in the  $v > 0$  half plane set  $y(w, \bar{U}) = w'(\xi)$ . Then  $y$  satisfies

$$A y \frac{dy}{dw} + Uy + Dy^2 + p(w) - p(w_-) = 0 , \quad (4.7)$$

$$y(w^*(\bar{U}), \bar{U}) = 0 . \quad (4.8)$$

From (4.7) we have

$$\begin{aligned} y^2(w, \bar{U}) &= -\frac{2}{A} \bar{U} \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) y(\zeta, \bar{U}) d\zeta \\ &\quad - \frac{2}{A} \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) f(\zeta, \bar{U}) d\zeta . \end{aligned}$$

Thus for  $w^*(\bar{U}) < w < w_+(\bar{U})$  we have

$$\begin{aligned} \eta^2(w, U) - y^2(w, \bar{U}) - \eta^2(w^*(\bar{U}), \bar{U}) &= \\ &\quad - \frac{2}{A} \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) (\eta(\zeta, U) - \bar{U}y(\zeta, U)) d\zeta \\ &\quad - \frac{2}{A} \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) (f(\zeta, U) - f(\zeta, \bar{U})) d\zeta \end{aligned}$$

where  $\eta(w, U)$  satisfies (4.3), (4.4). Thus we find

$$\begin{aligned} \eta^2(w, U) - y^2(w, \bar{U}) - \eta^2(w^*(\bar{U}), \bar{U}) &= \\ &\quad - \frac{2}{A} (U - \bar{U}) \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) \eta(\zeta, U) d\zeta \\ &\quad - \frac{2}{A} \bar{U} \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) (\eta(\zeta, U) - y(\zeta, \bar{U})) d\zeta \\ &\quad - \frac{2}{A} (U^2 - \bar{U}^2) \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) (\zeta - w_-) d\zeta . \end{aligned}$$

Now if  $\eta(z, U) - y(z, \bar{U}) < 0$  for some  $z, w^*(\bar{U}) < z < w_+(\bar{U})$ , we have

$\gamma_U^+(w_-, 0)$  entering  $\Omega_{\bar{U}} \subset \Omega_U$  and we can use Lemma 4.6 to obtain the result.

On the other hand if  $\eta(\zeta, U) - y(\zeta, \bar{U}) > 0$  on  $[w^*(\bar{U}), w_+(\bar{U})]$  then

$$\begin{aligned} \eta^2(w, U) - y^2(w, \bar{U}) - \eta^2(w^*(\bar{U}), \bar{U}) &< \\ &\quad - \frac{2}{A} (U - \bar{U}) \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) \eta(\zeta, U) d\zeta + \text{const.} |U^2 - \bar{U}^2| , \end{aligned}$$

where const. depends only on  $w^*(\bar{U})$  and  $w_+(\bar{U})$ . From Lemma 4.4

$\eta(\zeta, \bar{U}-\epsilon) > \eta(\zeta, U) > 0$  on  $(w_-, \tilde{w}(U))$ . Since we assume  $\eta(\zeta, U) > y(\zeta, \bar{U})$  on  $[w^*(\bar{U}), w_+(\bar{U})]$  and we know  $y(\zeta, \bar{U}) > 0$  on  $[w^*(\bar{U}), w_+(\bar{U})]$  we must have  $w_+(\bar{U}) < \tilde{w}(U)$ . Thus  $(w_-, \tilde{w}(U))$  must contain  $[w^*(\bar{U}), w_+(\bar{U})]$  and therefore

$$\begin{aligned}
& \eta^2(w, U) - y^2(w, \bar{U}) - \eta^2(\bar{w}, \bar{U}) < \\
& - \frac{2}{A} (U - \bar{U}) \int_{w^*(\bar{U})}^w \exp\left(\frac{2D}{A} (\zeta - w)\right) \eta(\zeta, \bar{U} - \varepsilon) d\zeta \\
& + \text{const.} |U^2 - \bar{U}^2| < \text{const.} |U - \bar{U}| , \tag{4.9}
\end{aligned}$$

on  $[w^*(\bar{U}), w_+(\bar{U})]$ . So if we can show  $\eta^2(w^*(\bar{U}), U) < \text{const.} |U - \bar{U}|$  we will have  $0 < \eta^2(w, U) - y^2(w, \bar{U}) < \text{const.} |U - \bar{U}|$  on  $[w^*(\bar{U}), w_+(\bar{U})]$ . Hence for  $-\varepsilon < U - \bar{U} < 0$  and  $\varepsilon > 0$  sufficiently small,  $\gamma_U^+(w_-, 0)$  must enter  $\Omega_{\bar{U}} \subset \Omega_U$  and Lemma 4.6 will imply the result. As advertised above to conclude the proof we need to estimate  $\eta^2(w^*(\bar{U}), U)$ . From (4.5) we have

$$\begin{aligned}
\eta^2(w^*(\bar{U}), U) &= \eta^2(w^*(\bar{U}), U) - \eta^2(w^*(\bar{U}), \bar{U}) = \\
&- \frac{2}{A} U \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta, w)\right) \eta(\zeta, U) d\zeta - \frac{2}{A} \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta, w)\right) f(\zeta, U) d\zeta \\
&+ \frac{2}{A} \bar{U} \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) \eta(\zeta, \bar{U}) d\zeta + \frac{2}{A} \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) f(\zeta, \bar{U}) d\zeta \\
&= - \frac{2}{A} \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) (U\eta(\zeta, U) - \bar{U}\eta(\zeta, \bar{U})) d\zeta \\
&- \frac{2}{A} (U^2 - \bar{U}^2) \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) (\zeta - w_-) d\zeta \\
&= - \frac{2}{A} \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) [(U - \bar{U})\eta(\zeta, U) + \\
&\quad \bar{U}(\eta(\zeta, U) - \eta(\zeta, \bar{U}))] d\zeta \\
&- \frac{2}{A} (U^2 - \bar{U}^2) \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) (f - w_-) d\zeta .
\end{aligned}$$

Since  $\eta(\zeta, \bar{U} - \varepsilon) > \eta(\zeta, U) > \eta(\zeta, \bar{U}) > 0$  on  $(w_-, w^*(\bar{U}))$  we see

$$\begin{aligned}
\eta^2(w^*(\bar{U}), U) &< - \frac{2}{A} (U - \bar{U}) \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) \eta(\zeta, \bar{U} - \varepsilon) d\zeta \\
&- \frac{2}{A} (U^2 - \bar{U}^2) \int_{w_-}^{w^*(\bar{U})} \exp\left(\frac{2D}{A} (\zeta - w)\right) (\zeta - w_-) d\zeta
\end{aligned}$$

and hence  $\eta^2(w^*(\bar{U}), U) < \text{const.} |U - \bar{U}|$ . The proof is now complete. □

Lemma 4.10. Assume there exists  $U_1 > 0$  so that the orbit  $\gamma_{U_1}^+(w_-, 0)$  of (3.8) has  $(w_+(U_1), 0)$  as its  $\omega$ -limit set. Then there exists  $\epsilon > 0$  so that if  $-\epsilon < U_2 - U_1 < 0$  then  $\gamma_{U_2}^+(w_-, 0)$  has  $(w_+(U_2), 0)$  as its  $\omega$ -limit set.

Proof. Since  $\Omega_{U_1} \subset \Omega_{U_2}$  and  $\gamma_U^+$  is continuous with respect to  $U$ , we know  $\gamma_{U_2}^+(w_-, 0)$  will enter  $\Omega_{U_2}$  for  $U_2$  near  $U_1$ . Now use Lemma 4.6.  $\square$

Lemma 4.11. Assume there exists  $\bar{U} > 0$  so that there is a solution of (3.8) connecting the saddle  $(w_-, 0)$  with the saddle  $(w^*(\bar{U}), 0)$  in the  $v > 0$  half plane,  $w^*(\bar{U}) < w_+(\bar{U})$ . Then if  $A > \frac{1}{8}$  we have for all  $U$ ,  $0 < U < \bar{U}$ ,  $\gamma_U^+(w_-, 0)$  has  $(w_+(U), 0)$  as its  $\omega$ -limit set.

Proof. From Lemmas 4.9 and 4.10 we know the conclusion of Lemma 4.11 will be true unless there is a decreasing sequence  $\{U_n\}$ ,  $U_n > 0$  and  $U^* > 0$  so that

$$U_n \searrow U^* \text{ as } n \rightarrow \infty ,$$

$(w_+(U_n), 0)$  is in the  $\omega$ -limit set of  $\gamma_{U_n}^+(w_-, 0)$ ,

$(w_+(U^*), 0)$  is not in the  $\omega$ -limit set of  $\gamma_{U^*}^+(w_-, 0)$ .

From Lemma 4.2 we know  $n(w, U^*)$  is bounded on  $(w_-, \tilde{w}(U^*))$  by some constant  $K(U^*)$ . By Lemma 4.4 we know  $n(w, U_n)$  is bounded by  $K(U^*)$  on  $(w_-, \tilde{w}(U_n))$ ,  $U^* < U_n < U_1$ . Since  $\tilde{w}(U_n) = w_+(U_n)$  we have  $n(w, U_n)$  bounded by  $K(U^*)$  on  $(w_-, w_+(U_n))$ . From (4.5) we have on  $(w_-, w_+(U_n))$

$$\begin{aligned} 0 &< n^2(w, U^*) - n^2(w, U_n) = \\ &\quad \frac{2}{A} \int_{w_-}^w \exp\left(\frac{2D}{A}(\zeta - w)\right) [(U_n - U^*)(n(\zeta, U^*) - n(\zeta, U_n)) \\ &\quad - (U_n n(\zeta, U^*) - U^* n(\zeta, U_n))] d\zeta \\ &\quad - \frac{2}{A} (U^* - U_n)^2 \int_{w_-}^w \exp\left(\frac{2D}{A}(\zeta - w)\right) (\zeta - w) d\zeta . \end{aligned}$$

By Lemma 4.4  $U_n n(\zeta, U^*) - U^* n(\zeta, U_n) > 0$  on  $(w_-, w_+(U_n))$  and since we have

the bound  $K(U^*)$  on  $\eta(\zeta, U^*)$  and  $\eta(\zeta, U_n)$  (both of which are positive on  $(w_-, w_+(U_n))$ ) we see  $0 < \eta^2(w, U^*) - \eta^2(w, U_n) < \text{const. } |U_n - U^*|$  on  $(w_-, w_+(U_n))$ . Now let  $w \rightarrow w_+(U_n)$ . Since  $\eta^2(w_+(U_n), U_n) = 0$  we have  $0 < \eta^2(w_+(U_n), U^*) < \text{const. } |U_n - U^*|$  and so  $\eta^2(w_+(U_n), U^*) \rightarrow 0$  as  $U_n \rightarrow U^*$ . Also since  $w_+(U_n) \rightarrow w_+(U^*)$  as  $U_n \rightarrow U^*$  it follows that  $(w_+(U^*), 0)$  is in the  $w$ -limit set of  $\gamma_{U^*}^+(w_-, 0)$ . This is the desired contradiction and the lemma is proven.  $\square$

Lemma 4.12. Assume  $A > 0$  and let  $w_-$  be such that either

$$(I) \quad \int_{w_-}^{w^*(0)} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, 0) d\zeta < 0, \quad \gamma < w_- < \alpha,$$

or

$$(I') \quad b < w_- < \gamma,$$

and

(II) assume there exists  $U_M > 0$  so that

$$\int_{w_-}^{w^*(U_M)} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, U_M) d\zeta = 0.$$

Then there exists a  $\bar{U}$ ,  $0 < \bar{U} < U_M$  so that (3.8) possesses a solution in the  $v > 0$  half plane connecting the saddles  $(w_-, 0)$  and  $(w^*(\bar{U}), 0)$ .

Proof. From (4.5) we know

$$\eta^2(w, U) = -\frac{2U}{A} \int_{w_-}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) \eta(\zeta, U) d\zeta$$

$$-\frac{2}{A} \int_{w_-}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) f(\zeta, U) d\zeta$$

where  $\eta$  satisfies (4.3), (4.4).

For  $U = 0$ ,

$$\eta^2(w, 0) = -\frac{2}{A} \int_{w_-}^w \exp\left(\frac{2D}{A}(\zeta-w)\right) f(\zeta, 0) d\zeta.$$

If (I') holds  $f(\zeta, 0) = p(\zeta) - p(w_-) < 0$  and  $\eta^2(w, 0) > 0$ . If (I) holds (H1)-(H6) imply again  $\eta^2(w, 0) > 0$ . So the orbit exiting  $(w_-, 0)$  for (3.8) in the  $v > 0$  half plane never crosses the  $w$  axis. On the other hand

$$\begin{aligned}\eta^2(w^*(U_M), U_M) &= -\frac{2U_M}{A} \int_{w_-}^{w^*(U_M)} \exp\left(\frac{2D}{A}(\zeta-w)\right) \eta(\zeta, U_M) d\zeta \\ &\quad - \frac{2}{A} \int_{w_-}^{w^*(U_M)} \exp\left(\frac{2D}{A}(\zeta-w)\right) f(\zeta, U_M) d\zeta \\ &= -\frac{2U_M}{A} \int_{w_-}^{w^*(U_M)} \exp\left(\frac{2D}{A}(\zeta-w)\right) \eta(\zeta, U_M) d\zeta\end{aligned}$$

which implies  $\eta(\zeta, U_M) = 0$  for some  $\zeta$ ,  $w_- < \zeta < w^*(U_M)$ . By continuity with respect to  $U$  we see that for some  $U$ ,  $0 < U < U_M$ ,  $\eta(w^*(U), U) = 0$ . The proof is complete.  $\square$

Proof of Theorem 4.1. Part (i) follows from Lemma 4.12. Part (ii) is a consequence of Lemmas 4.10, 4.11 and 4.12.  $\square$

We now give a mechanistic interpretation of Theorem 4.1. Let us assume  $A > \frac{1}{8}$  and  $w_-$  is such that (I) or (I') and (II) hold. If we look on the Hugonot curve (Figure 9) we see for  $w_+(U_a) > w_+(\bar{U})$ ,  $0 < U_a < \bar{U}$ , (4.2) with  $U = U_a$  gives the solution of the Riemann problem (1.6) with Cauchy data

$$\begin{cases} w = w_- & w = w_+(U_a) \\ u = u_+ + U_a(w_+(U_a) - w_-) & u = u_+ \end{cases} \quad \begin{matrix} x < 0, & x > 0 \\ \end{matrix} . \quad (4.10)$$

This solution is admissible according to the viscosity - capillarity criterion  $(A, D)$ ,  $A > \frac{1}{8}$ . A representation of the solution  $x - t$  plane is given in Figure 10.

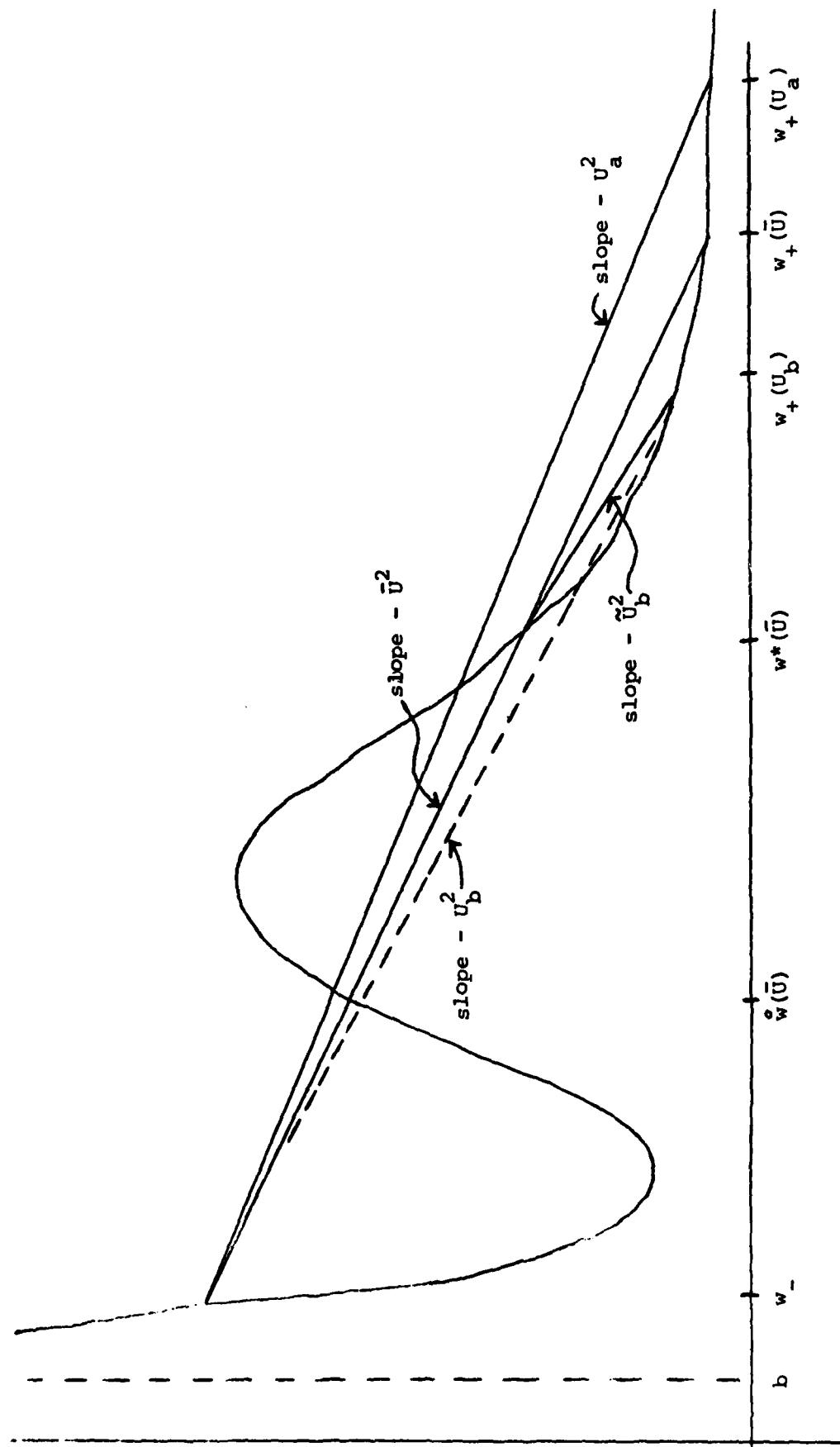


Figure 9

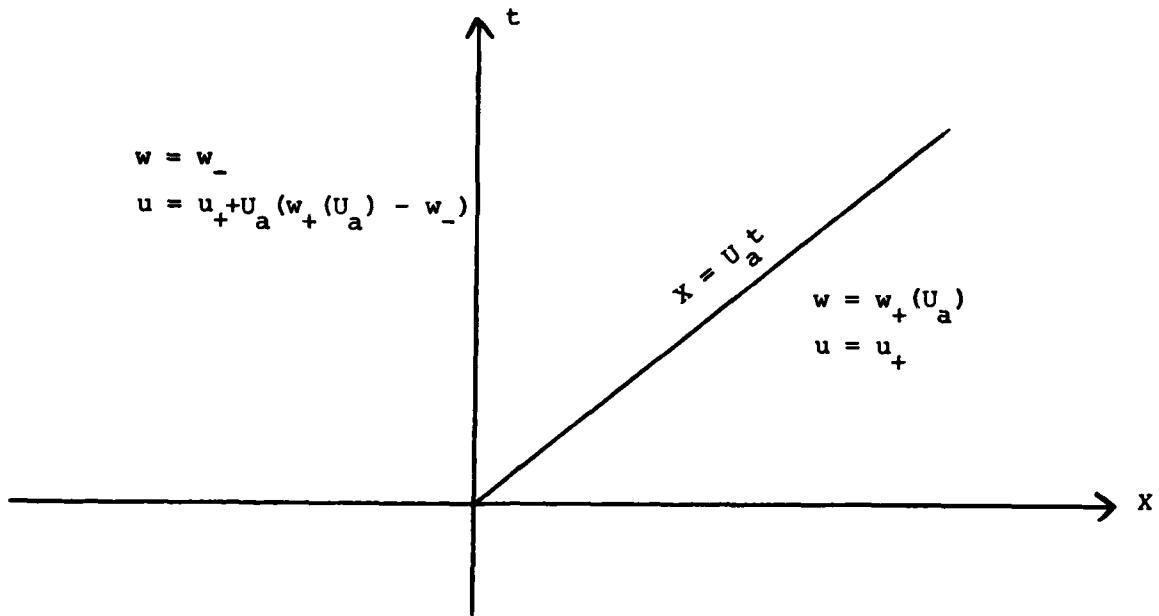


Figure 10: Solution of (1.6), (4.10)

As we compress the fluid so that  $w^*(\bar{U}) < w_+(U_b) < w_+(\bar{U})$  for some  $U_b$ ,  $U_b > \bar{U} > 0$ , the admissibility of the above solution is no longer guaranteed by Theorem 4.1. For example we see the Riemann problem for Cauchy data

$$\begin{cases} w = w_- \\ u = u_+ + \tilde{U}_b (w_+(U_b) - w^*(\bar{U})) + \bar{U}(w^*(\bar{U}) - w_-) \end{cases} \quad \begin{cases} x < 0, \\ x > 0 \end{cases} \quad (4.11)$$

possesses a solution (see Figure 11)

$$\begin{aligned} w &= w_- \\ u &= u_+ + \tilde{U}_b (w_+(U_b) - w^*(\bar{U})) + \bar{U}(w^*(\bar{U}) - w_-) \quad x < \bar{U}t, \\ w &= w^*(\bar{U}) \\ u &= u_+ + \tilde{U}(w_+(U_b) - w^*(\bar{U})) \quad \bar{U}t < x < \tilde{U}t, \\ w &= w_+(U_b), \\ u &= u_+ \end{aligned} \quad (4.12)$$

where

$$U_b = +\sqrt{\frac{-p(w_+(U_b)) + p(w_-)}{w_+(U_b) - w_-}},$$

$$\tilde{U} = +\sqrt{\frac{-p(w^*(\bar{U})) + p(w_+(U_b))}{w^*(\bar{U}) - w_+(U_b)}},$$

$$\bar{U} = +\sqrt{\frac{-p(w^*(\bar{U})) + p(w_-)}{w^*(\bar{U}) - w_-}}.$$

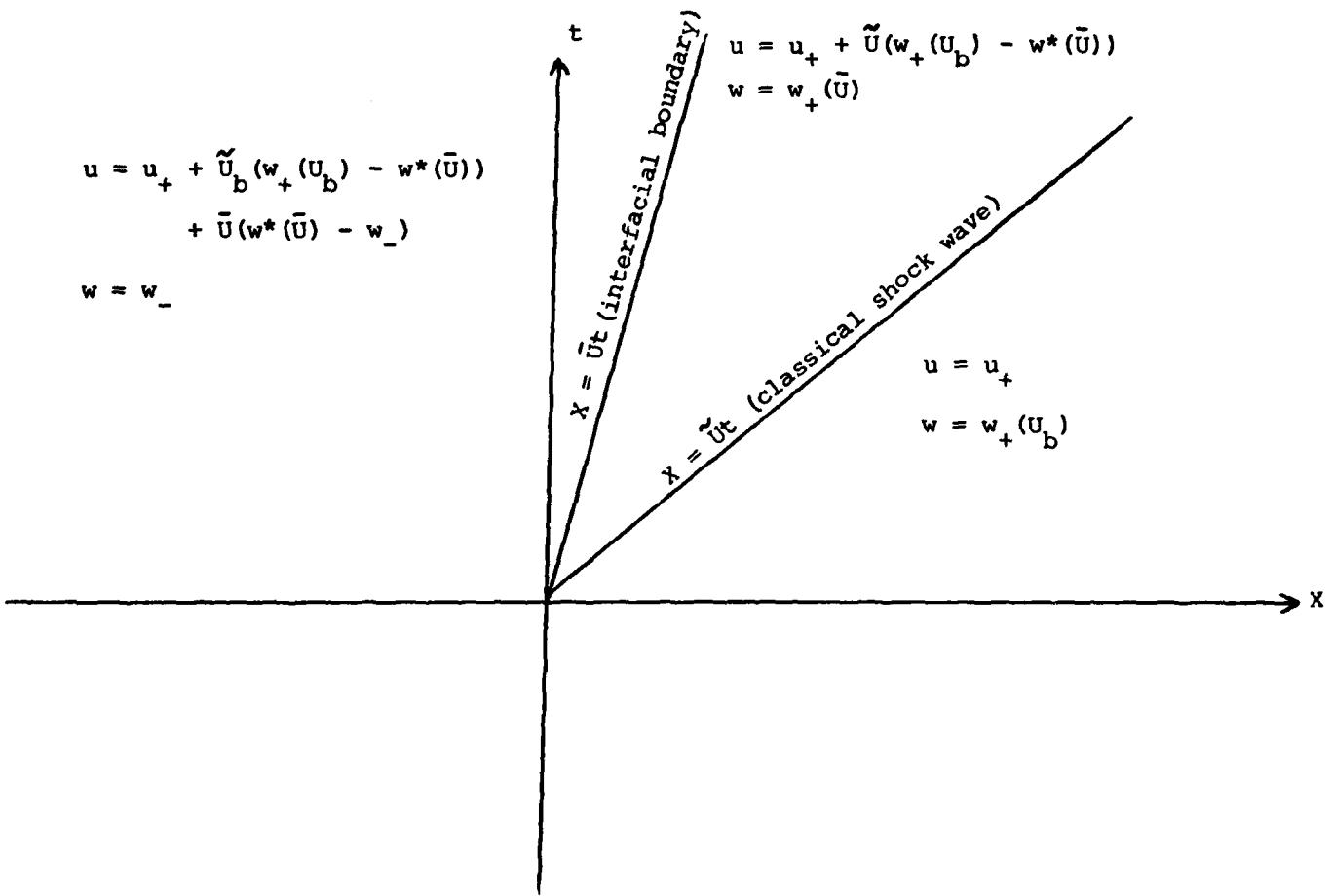


Figure 11: Solution of (1.6), (4.11)

From Theorem 4.1 and Theorem 3.3 (i) we see the solution is admissible according to the viscosity-capillarity condition  $(A,D)$ ,  $A > \frac{1}{8}$  in that both  $x = \bar{U}t$  and  $x = \tilde{U}t$  are admissible singular surfaces. Such a solution indicates that as the fluid is compressed for  $w_+(U_a) > w_+(\bar{U})$  a single propagating phase boundary, separating liquid and vapor phases, and traveling with speed  $U_a > 0$  is possible. However upon further compression  $w_+(U_b) < w_+(\bar{U})$ , this interface bifurcates into a classical shock in the vapor phase moving out from the propagating interface. The shock travels with speed  $\tilde{U}$ , the liquid-vapor interface now travels with fixed speed  $\bar{U}$ . Thus  $\bar{U}$  represents the maximum speed a liquid-vapor interface may travel in compression (see Figure 12).

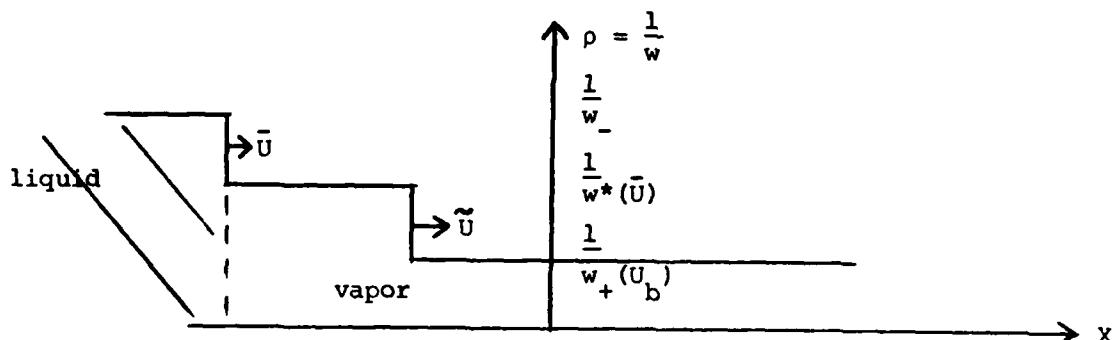
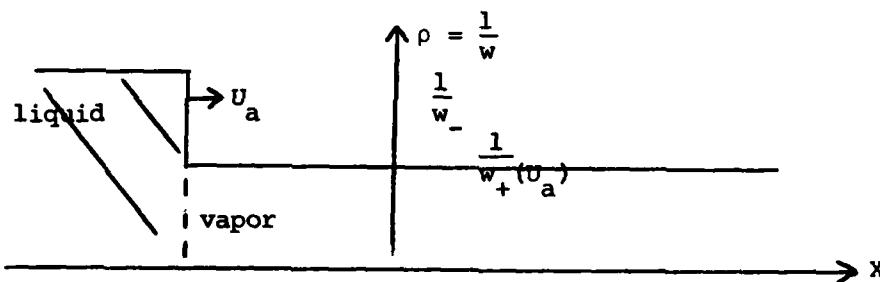


Figure 12: Shock wave bifurcates out of liquid vapor interface,  $U_a < \bar{U} < U_b$ .

On the other hand if we reverse the process and start with initial data (4.11) and raise  $w_+(U_b)$  through expansion the shock wave and interfacial boundary of (4.12) will coalesce into an interfacial boundary traveling with speed  $U_a$ .

Example 12. Let  $w_+$  be given in  $(\beta, \infty)$  and let  $w_-(U)$  be a solution of the Rankine-Hugoniot relation with  $U < 0$ , namely

$$U = -\sqrt{\frac{-p(w_+) + p(w_-(U))}{w_+ - w_-(U)}} .$$

In this case an argument similar to that given for Lemma 4.12 yields the following result.

Theorem 4.13. Assume  $A > 0$  and let  $w_+$  be such that either

$$(I) \quad \int_{w_-(0)}^{w_+} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, 0) d\zeta > 0 \quad \beta < w_+ < \delta ,$$

or

$$(I') \quad \delta < w_+ ,$$

and

(II) assume there exists  $U_M < 0$  so that

$$\int_{w_-(U_M)}^{w_+} \exp\left(\frac{2D}{A}\zeta\right) f(\zeta, 0) d\zeta = 0 .$$

Then there is a unique  $\bar{U}$ ,  $U_M < \bar{U} < 0$ , so that (3.8) possesses a solution in the  $v < 0$  half-plane connecting  $(w_-(\bar{U}), 0)$  to  $(w_+, 0)$ .

Pictorially this result is represented in Figures 13 and 14. In this case the singular surface  $X = \bar{U}t$  separating liquid and vapor phases is a rarefaction shock which is admissible according to the viscosity-capillarity condition (A,D). This example stands in contrast to Example 9 where the interfacial rarefaction shock was not (modulo exceptional circumstances) admissible according to the viscosity-capillarity condition (A,D).

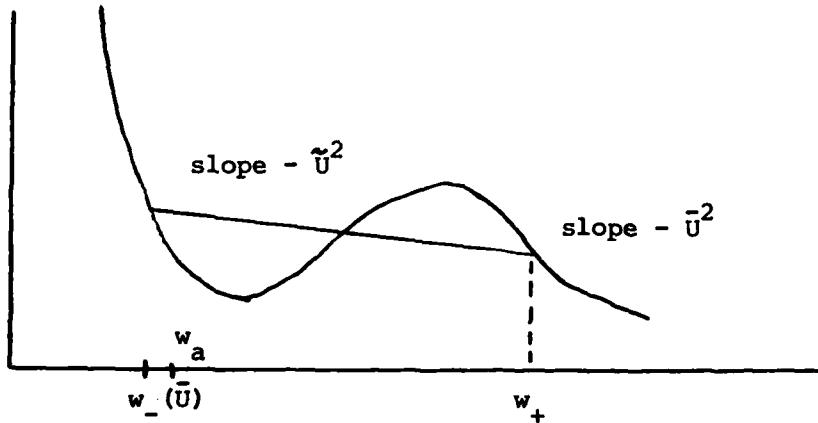


Figure 13

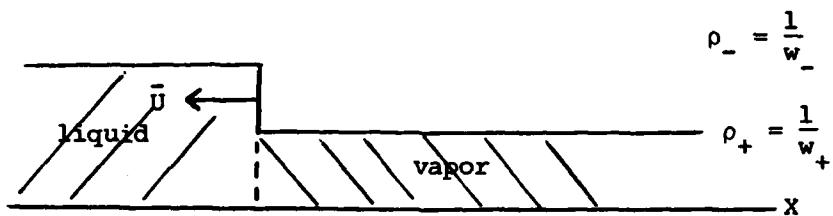


Figure 14: Rarefaction shock waves

If the fluid is compressed or expanded at  $x = -\infty$  changing to value of  $w_-$

(U) the pure rarefaction will disappear. Expansion will set new Cauchy data

e.g. if  $w_-(\bar{U}) < w_a < a$ ,

$$\begin{aligned} w &= w_a & x < 0 & , \quad w = w_+ & x > 0 \\ u &= u_- & & u = u_- + \tilde{U}(w_-(\bar{U}) - w_a) + \bar{U}(w_+ - w_-(\bar{U})) & (4.13) \end{aligned}$$

then (1.5) possesses a solution

$$w = w_a \quad x < \tilde{U}t ,$$

$$u = u_-$$

$$w = w_-(\bar{U})$$

$$\tilde{U}t < x < \bar{U}t ,$$

(4.14)

$$u = u_- + \tilde{U}(w_-(\bar{U}) - w_a)$$

$$w = w_+$$

$$\bar{U}t < x$$

$$u = u_- + \tilde{U}(w_-(\bar{U}) - w_a) + \bar{U}(w_+ - w_-(\bar{U})) .$$

$$\text{Here } \tilde{U} = \sqrt{\frac{-p(w_-(\bar{U})) + p(w_a)}{w_-(\bar{U}) - w_a}} .$$

Of course from Theorems 3.3 and 4.13 will show (4.14) is admissible according to the viscosity-capillarity criterion (A,D).

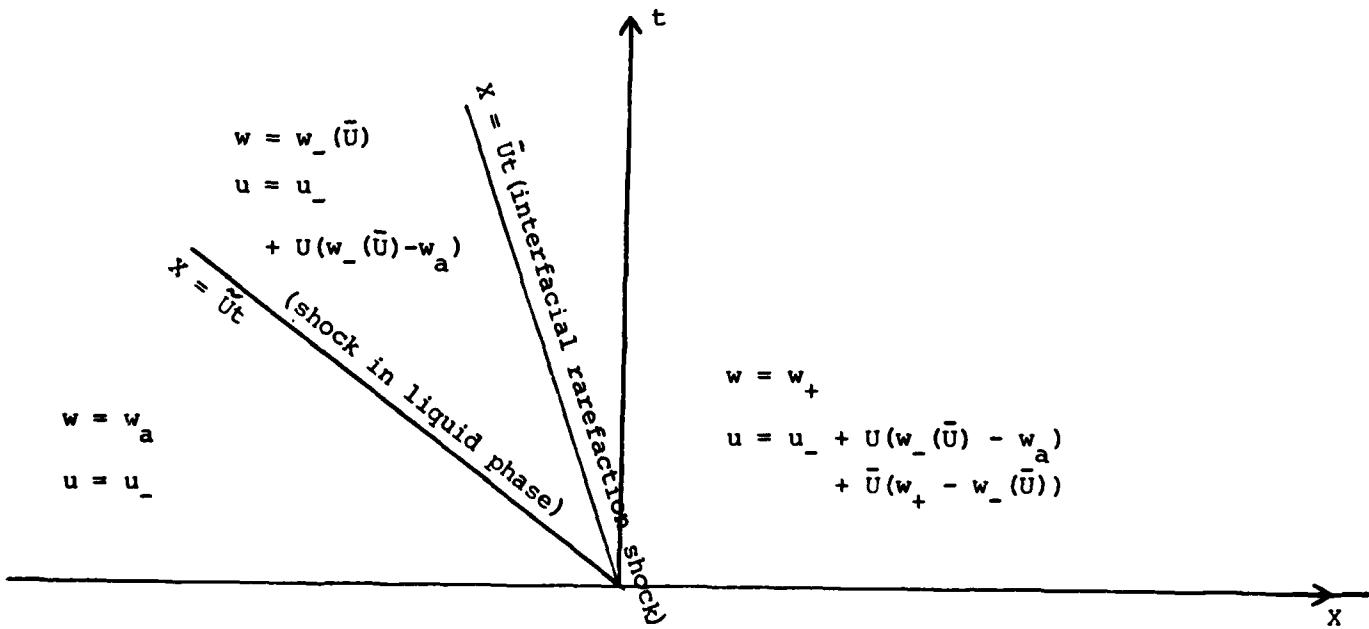


Figure 15

On the other hand if we compress the fluid at  $+ \infty$  we can envisage

Cauchy data

$$\begin{aligned} w &= w_b & x < 0, & w = w_+ & x > 0 \\ u &= u_- & & u = u_+ & \end{aligned} \quad (4.15)$$

where  $b > w_b < w_-(\bar{U})$ . In this case we again can connect the vapor state  $w = w_+$ ,  $u = u_+$  to a liquid phase  $w = w_-(\bar{U})$ ,  $u = u_+ - \bar{U}(w_+ - w_-)(\bar{U})$ . Then this liquid phase can be connected by a classical rarefaction wave in the liquid phase to  $w = w_b$ ,  $u = u_-$  for  $w_b, u_-$  sufficiently near  $w_-(\bar{U})$ ,  $u_+ - \bar{U}(w_+ - w_-)(\bar{U})$  (see Lax [16]). Pictorially the result is shown in Figure 16.

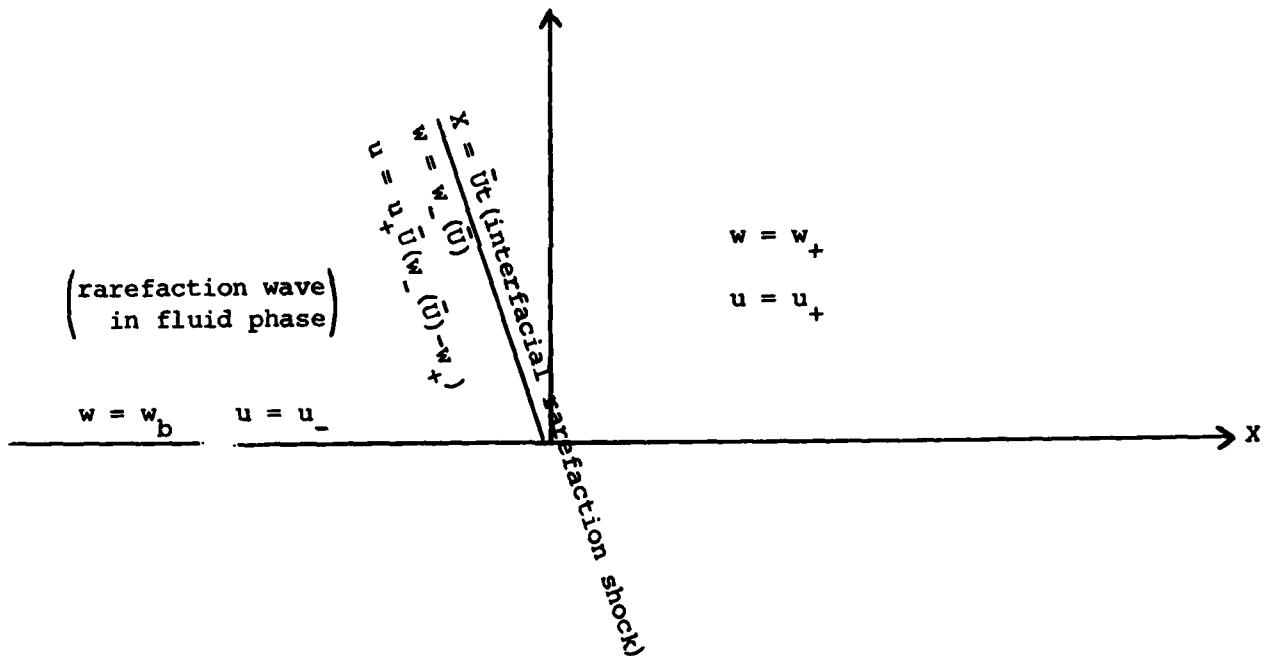


Figure 16

Example 13. In this example we see that "metastable" states are dynamically admissible as perturbations of an equilibrium configuration. Assume  $u_- = u_+ = 0$ ,  $U = 0$ , and  $w_-$  and  $w_+$

$$\int_{w_-}^{w_+} \exp(\frac{2D}{A}\zeta) (p(\zeta) - p(w_-)) d\zeta = 0 .$$

Hence according to Example 10 this singular surface is admissible according to the viscosity-capillarity condition (A,D). But from Theorem 3.3 (i) the singular surfaces

$$\Gamma_1 : x = U_a t \text{ separating } w = w_+, u = 0 \text{ and}$$

$$w = w_a, u = -U_a (w_+ - w_a) \text{ with } \beta < w_a < w_+ \text{ and}$$

$$U_a = + \sqrt{\frac{-p(w_+) + p(w_a)}{w_+ - w_a}},$$

$$\Gamma_2 : x = U_b t \text{ separating } w = w_-, u = 0 \text{ and}$$

$$w = w_b, u = -U_b (w_- - w_b) \text{ with } w_- < w_b < \alpha \text{ and}$$

$$U_b = - \sqrt{\frac{-p(w_b) + p(w_-)}{w_b - w_-}}$$

are admissible according to the viscosity-capillarity criterion (A,D),  $A > 0$ .

Thus the Cauchy problem (1.6) with initial data

$$\begin{array}{ll} w = w_- & w = w_a \\ x < 0 & , \\ u = 0 & u = -U_a (w_+ - w_a) \end{array} \quad (4.16)$$

and

$$\begin{array}{ll} w = w_b & w = w_+ \\ x < 0 & , \\ u = -U_b (w_- - w_b) & u = 0 \end{array} \quad (4.17)$$

possesses solutions

$$\begin{array}{lll} w = w_- & w = w_+ & w = w_a \\ x < 0, & 0 < x < U_a t, & x > U_a t \\ u = 0 & u = 0 & u = -U_a (w_+ - w_a) \end{array} \quad (4.18)$$

$$\begin{aligned}
 w &= w_b & w &= w_- & w &= w_+ \\
 x < U_b t, & & U_b t < x < 0, & & x > 0. & (4.19) \\
 u = -U_b (w_- - w_b) & & u = 0 & & u = 0
 \end{aligned}$$

By Theorem 3.3 (i) and Example 10 these solutions are admissible according to the viscosity-capillarity condition  $(A, D)$ ,  $A > 0$ . (See Figure 17.)

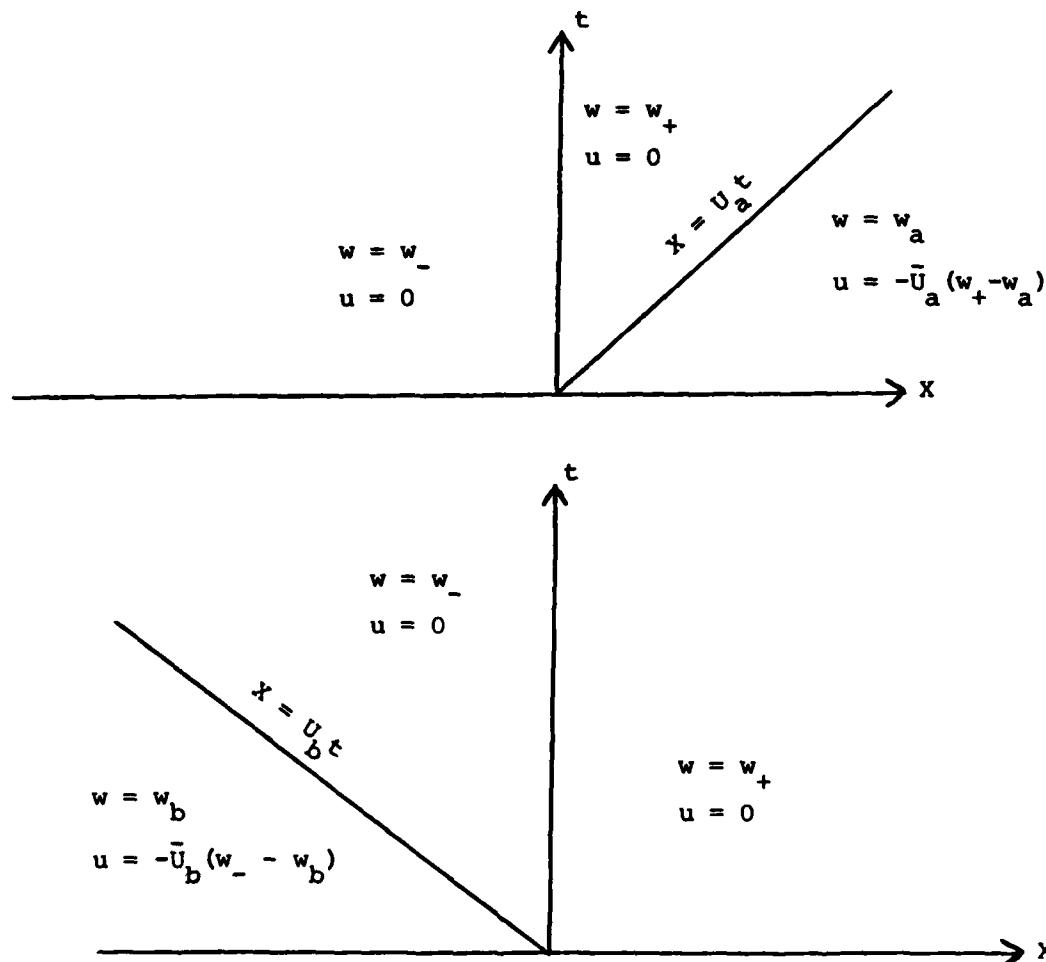


Figure 17: Solution 4.18 above and 4.19 below

In both examples we see solutions exist in the "metastable" regions  $(w_-, \alpha)$  and  $(\beta, w_+)$  though only for a period of finite duration determined by  $U_a$  and  $U_b$  respectively.

Remarks. The results presented in this section are consistent with those given by Zel'dovich and Raizer [17, p. 750-762]. However unlike the purely physical arguments given there our results are based on a rigorous analysis of the "shock structure problem". Moreover we note that the result of Theorem 4.1 (i) showing the theoretical existence of a shock wave (admissible in the sense of the capillarity-viscosity criterion  $(A,D)$ ,  $A > 0$ ) for the complete transition from superheated vapor to liquid is consistent with the experimental results of Dettleff, Thompson, Meier, and Speckman [18]; see [5] for a complete non-isothermal discussion of this result.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  This paper considers admissibility criteria for non-linear conservation laws based on (i) viscosity and (ii) capillarity and viscosity. It is shown by means of specific examples that while (ii) yields results consistent with experiment for materials exhibiting phase transitions, e.g. a van der Waals fluid, (i) does not.		